Article

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Comparing Magnetism in Isostructural Oxides $\text{A}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$: Anisotropic Spin Glass (A = Ba) Versus Long Range Order (A = Sr)

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Abstract

This study presents the strikingly distinct magnetic properties of two isostructural compounds, $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ and $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ (K_2NiF_4 – type, $I4/mmm$). Spectroscopic studies have shown that Mn is in a +3.0(1) oxidation state only, in both compounds; therefore, the charge is balanced by accommodating extra oxygen at interstitial sites, as confirmed by neutron powder diffraction. We found that the Ba compound exhibits an exceedingly rare anisotropic spin glass behaviour, $T_g = 26.4$ K, with the moment freezing along the c -axis only while the in-plane spin components remain dynamic well below T_g . Experimental results including neutron diffraction, heat capacity, and magnetic (dc and ac) measurements performed on an oriented single crystal support this conclusion. This is a remarkable result, the only other known example of an anisotropic spin glass being Fe_2TiO_5 . The spin glass state in $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ is argued to arise due to competing antiferromagnetic and ferromagnetic 180° $\text{Mn}^{3+}\text{--O--Mn}^{3+}$ superexchange interactions. In contrast, the Sr analogue shows 2D antiferromagnetic correlations and long range antiferromagnetic order below 95 K with a remarkably reduced ordered moment of $1.4 \mu_B/\text{Mn}^{3+}$ instead of the $\sim 4 \mu_B$ expected for an $S = 2$ ion.

Introduction

Materials with the K_2NiF_4 structure have been of considerable interest since the 1950's [1] while low dimensional magnetism was one of the original foci through the 1970's and beyond [2,3]. The discovery of high temperature superconductivity in doped La_2CuO_4 and oxygenated $La_2CuO_{4+\delta}$ launched an enormous literature. Other oxides with the K_2NiF_4 -type structure such as La_2NiO_4 , $LaSrNiO_4$ and $LaSrMnO_4$ have since then attracted interest and found potential applications as magnetic sensors and cathode materials for high temperature solid oxide fuel cells [4,5].

The K_2NiF_4 type-oxides can also be described as $n = 1$ members of the Ruddlesden-Popper family of oxides, $AO(ABO_3)_n$, wherein layers of rock salt (AO) inter-grow with layers of perovskite (ABO_3). The A-site can be occupied by a large divalent or trivalent cation such as Sr^{2+} , Ba^{2+} or La^{3+} and the B-site by a magnetic transition metal ion with either +2,+3 or +4 oxidation state, depending on the A-site – **Figure 1a**.

Figure 1 (a) The unit cell of a A_2BO_4 oxide, $BaLaMnO_4$, with the $n = 1$ RP phase (K_2NiF_4) structure. The grey and red spheres are the A and O ions, respectively, and the B ion, green, occupies a tetragonally elongated octahedral site. (b) The body centred tetragonal B sublattice formed by the Mn ions (green spheres), showing the condition for interplanar spin frustration. (c) The inter-layer magnetic exchange paths with the associated coupling constants, J^{inter} and J_0 . While the intra planar magnetic exchange in the ab plane (blue) is simple, the interplanar magnetic exchange path (in purple) is more complex involving three mediating ions and an angle of about 120° .

It is of great interest to study compounds with the K_2NiF_4 -type structure containing paramagnetic ions such as Mn^{3+} (a $3d^4$ ion with $t_{2g}^3e_g^1$ configuration). In such layered materials, frustration results due to the interlayer magnetic coupling in the Mn^{3+} sublattice of square planar layers stacked in an I -centred sequence – **Figure 1b**. As it can be seen from **Figure 1c**, the

magnetic exchange between the Mn^{3+} ions in the ab plane is simple since the $\text{Mn}^{3+}\text{--O--Mn}^{3+}$ path is linear. However, the magnetic exchange is complicated between the planes since it involves three mediating atoms and an angle of about 120° . Because of that, the sign for the exchange coupling is difficult to predict and only weak couplings are expected.

Additionally, compounds containing Mn^{3+} show a static Jahn-Teller deformation evidenced by the two sets of Mn–O bond distances. The K_2NiF_4 structure also allows the accommodation of an oxygen excess within the AO layers. Such an excess of oxygen could be balanced by changing the oxidation state of the B-site cation resulting in mixed ionic-electronic conductors [6].

One well-known example - SrLaMnO_4 - shows antiferromagnetic order and a $T_N = 128$ K with a magnetic wave vector $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, 0)$ [7,8,9], $a_{\text{mag}} = \sqrt{2} \cdot a_{\text{cryst}}$. On the other hand, quite surprisingly, less is known about the magnetic ground state of the isostructural Ba-analogue, BaLaMnO_4 , due to a persistent ferromagnetic impurity which complicated the analysis [9]. In a very recent study using polarized neutrons [10] it was shown that the ground state is devoid of spin-spin correlations and that a transition in the susceptibility at 19.2 K is likely due to spin freezing.

Sr-rich solid solutions $\text{Sr}_{1+x}\text{La}_{1-x}\text{MnO}_4$, $0 \leq x < 0.7$, can form and their structural and magnetic properties are known [11,12,13]. Depending on the doping value, x , the magnetic properties of $\text{Sr}_{1+x}\text{La}_{1-x}\text{MnO}_4$ vary from three dimensional long range order to the disappearance of long range order in the intermediate region, followed by a complex antiferromagnetic order and a superstructural order at higher dopings.

In non-stoichiometric $\text{Sr}_{1+x}\text{R}_{1-x}\text{MnO}_4$ phases, with $\text{R} = \text{La}, \text{Pr}, \text{and Nd}$ and $0.2 \leq x \leq 0.6$, the coexistence of Mn^{3+} with Mn^{4+} gives rise to spin glass states, arising due to the competition between the antiferromagnetic superexchange interaction and ferromagnetic double-exchange interaction. Note that the spin glass transition was isotropic, both in the ab plane and along the c -axis, for the La-doped compounds, while the Nd- and Pr- compounds show more anisotropy which has been attributed to the influence of the magnetic rare earth ions [14].

While Sr-rich $\text{Sr}_{1+x}\text{La}_{1-x}\text{MnO}_4$ phases have been investigated, as described above, in the La-rich $\text{Sr}_{1-x}\text{La}_{1+x}\text{MnO}_4$ system only three compounds were reported so far: $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.0}$ (where Mn is in a mixed $3+/4+$ oxidation state), $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4-\delta}$ ($\delta = 0.06$) and $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4+\delta}$ with $\delta =$ up to 0.42 [15]. No information on a $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ which should contain 100% of Mn in $+3$ oxidation state is available so far. In the Ba-analogue system, no corresponding systems have been reported.

This work reports on the synthesis of two new isostructural compounds, $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4+\delta}$ and $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4+\delta}$ with $\delta \sim 0.1$ and compares their structural and magnetic properties. Initially, the intent was to grow a single crystal of stoichiometric BaLaMnO_4 . As described in the following text, the crystal which was actually grown had a composition near $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$. It is found that the magnetic properties of these two isostructural oxides differ radically, mirroring the differences reported recently for SrLaMnO_4 and BaLaMnO_4 [10].

Experimental

Synthesis of polycrystalline samples

$\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ and $\text{Ba}_{1-x}\text{La}_{1+x}\text{MnO}_{4+x/2}$ ($x = 0$ and 0.2) were prepared from SrCO_3 (99.999%, Cerac) BaCO_3 (99.999%, Cerac), La_2O_3 (99.9%, Cerac), and Mn_2O_3 (99.99%, Cerac). La_2O_3 and BaCO_3 were pre-fired at 1000 and 600 °C respectively, in air, to eliminate the residual water. Stoichiometric amounts of starting materials were ground and homogenised dry in a ball mill with Y-stabilised zirconia (YSZ) as a grinding agent. Pressed pellets were placed in an alumina boat on a bedding of the same material and fired at 800 °C for 12 h, followed by a temperature of 1350 °C for 36 h, in Ar atmosphere to avoid the formation of oxidized phases. The exact temperature, atmosphere, and length of reaction were found to be crucial in obtaining the right phase (avoiding the oxidation of Mn^{3+}) and without impurities. The as-prepared samples had a grey-blackish colour and were insulating.

The reactions that lead to the formation of the $(\text{Ba,Sr})_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ samples can be summarized as follows (**Equation 1**, $x = 0.2$):

Crystal growth

Polycrystalline BaLaMnO_4 was obtained by the method described above ($x = 0$). The powder was ground and pressed into rods with a diameter of 8 mm and a length of about 80 mm and sintered at 1350 °C/36 h, in Ar. Single crystals of $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4+\delta}$ were melt-grown from BaLaMnO_4 rods by using the floating zone method at a feeding speed of 15 mm/h, in Ar at 5 atmospheres pressure (5N purity). The obtained crystals were black and cleaved easily along the (001) plane.

X-ray powder diffraction

Laboratory X-ray powder diffraction data were obtained with a PANalytical X'Pert PRO (PANalytical, Almelo, Netherlands) with Cu-K α_1 radiation ($\lambda = 1.54056 \text{ \AA}$) and X'Celerator detector with a 2θ step of 0.0167° .

Laue diffraction

White beam (Laue) X-ray backscatter diffraction was used to assess the surface quality and to determine the orientation of the single crystals of the single crystal pieces taken from the larger crystal. The Laue diffraction patterns were acquired with the X-ray beam intercepting the crystal at different points.

Powder neutron diffraction

Neutron powder diffraction data were collected on the C2 diffractometer at the Canadian Neutron Beam Centre, NRC, Chalk River Laboratories. The measurements at Chalk River were performed at different temperatures: 6 K, 40, 70, 75, 80, 85 K, 90 K, 92 K, 93 K, 95 K, 100 K and 290 K for $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ and 3.5 K, 35 K and 295 K for $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$. The wavelength of the neutrons used for the measurements was $\lambda = 1.32876 \text{ \AA}$ and the 2θ range was $10\text{--}90$ degrees. The wavelength was calibrated by measuring the diffraction pattern of a standard powder of Al_2O_3 . The refinements were done with FullProf program suite [16] and GSAS-II [17]. Data were also collected at 300 K, at the Nanoscale Ordered Materials Diffractometer (NOMAD) at the Oak Ridge Laboratories. About 200 mg of sample were loaded into a 3 mm diameter quartz capillary. Reduction of the total scattering data to obtain the pair distribution function (PDF) was done with the PDFgetN software [18] using a Q_{max} of $25 \text{ \AA}^{-1}$. The data was analysed using the PDFgui [19] and RMCProfile software [20].

Elemental analysis

Samples of approximately 65 mg were dissolved in 5–10 mL of, freshly prepared, hot *aqua regia* and these concentrated solutions were diluted to 100 mL with distilled water. The elemental analysis was carried out using an ICPS (inductively coupled plasma spectrometer) ICP-Varian Vista Pro (software ICP Expert II) Fisher Scientific Instruments. Matrix matched standards, i.e. 10 ppm, Ba and La reference solutions dissolved in HNO_3 were used. The accuracy of the measurements is $\pm 5\%$ of the analyte.

Magnetic property measurements (dc and ac)

The magnetic susceptibility measurements were performed on both polycrystalline and single crystal samples using a Quantum Design MPMS SQUID magnetometer. The direct current (dc) zero-field cooled (ZFC) and field-cooled (FC) data were collected in the temperature range from 2 to 350 K and an applied magnetic field of 100 Oe. The polycrystalline samples were contained in gelatine capsules held in plastic straws. Empty gelatine capsules above and below the samples help to reduce background signal. The single crystals were fixed on a quartz rod. The high temperature measurements between 300 and 700 K were carried out in quartz tubes using a furnace inset. Hysteresis measurements were performed at 5 K with an applied field range of ± 50 kOe. The alternating current (ac) magnetic susceptibility were measured in the 2–100 K range at frequencies of 1, 10, 100, 500, 1000 Hz and with an ac amplitude of 3.5 Oe.

Heat capacity measurements

Heat capacity measurements were performed on single crystals of 3.5 mg. The single crystal was placed on a 8-wire sapphire platform stage of a Dynacool Physical Property Measurement System (Quantum Design). The single crystals were adhered to the platform using Apiezon N-grease during the measurements which were performed in a range of magnetic fields, from 0 to 9 kOe over the temperature range from 2 to 100 K. The heat capacity of the puck and grease were subtracted from the total heat capacity.

X-ray absorption near edge structure (XANES)

The valence state of Mn in the sample with the $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ and $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ composition, as well as reference compounds such as MnO, Mn_2O_3 , MnO_2 , BaLaMnO_4 , and $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4+\delta}$ (sample obtained in oxidising conditions) was investigated by using XANES. Mn K-edge absorption spectra was measured at room temperature, in transmission mode at the XAFS beamline of the ELETTRA synchrotron radiation facility in Trieste, Italy and at P65 beamline of PETRA III, DESY. The samples were pressed into pellets with the total absorption thickness (μd) of 2 above the investigated metal K-edge. A Si(111) double-crystal monochromator was used with an energy resolution of 0.8 eV at 7 keV. Higher-order harmonics were effectively eliminated by detuning the monochromator crystals to 60% of the rocking curve maximum at XAFS beamline. The intensity of the monochromatic X-ray beam was measured by using three consecutive long ionization detectors, filled with appropriate nitrogen and argon gas mixtures to obtain 15% absorption in the first cell and 70% in the second and

third cell. At XAFS beamline the absorption spectra were measured within the interval from -250 eV to $+1000$ eV relative to the Mn K $-$ edge. In the XANES region equidistant energy steps of 0.25 eV were used with the integration time of 1 s/step. At P65 beamline the absorption spectra were measured in the energy region from -150 eV to 1000 eV relative to the Mn K-edge in continuous and fast (3 min) scans and re-binned to the same energy steps in the XANES region. Three to six repetitions of the scans were superimposed to improve the signal-to-noise ratio. The exact energy calibration was established with a simultaneous absorption measurement on a 5 micron thick Mn metal foil placed between the second and the third ionization chamber. The Mn K-edge in the Mn metal is at 6539 eV. The absolute energy reproducibility of the measured spectra was 0.03 eV. Data analysis of XANES spectra was performed with Demeter (IFEFFIT) program package the Athena [21].

Bond valence calculations were carried out according to Brown [22], **Equations 2 and 3**:

$$S_i = \exp((R_i - R_0)/b) \quad (2)$$

$$V = \sum_i S_i \quad (3)$$

The bond valence S_i for bond i is determined from the bond distance R_i and tabulated R_0 values and with parameter $b = 0.37$. The bond valence sum V is the sum of all i bond valences S_i of the coordination sphere.

Results and Discussion

1 $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4+\delta}$

1.1 Single crystal growth results

The as-grown crystals are of black colour and have a metallic shiny appearance – please see **SI Figure 1**. The crystal habit is round with an elliptical contour.

1.2 Laue diffraction results

SI Figure 2a shows a typical crystal grown by the OFZ method oriented with the (001) plane facing the camera, which was confirmed by back-reflection Laue Diffraction. The same Laue patterns appear when measuring consecutive spots along the longitudinal axes of the crystal (**SI**

Figure 2b, c) indicating that the surface structure has a homogeneous orientation and composition.

1.3 Elemental analysis

The overall cation stoichiometry for the single crystals and the polycrystalline samples was investigated with inductively coupled plasma spectrometry (ICP). The total Ba^{2+} and La^{3+} concentrations are presented in the **SI Table 1**. From the elemental analysis it is suggested that the composition of the as-grown crystal is not stoichiometric but it is close to $\text{Ba}_{0.9}\text{La}_{1.1}\text{MnO}_{4.05}$. We believe that this difference in composition might have arisen due to some impurity or local inhomogeneity in the sample used for ICP. Chemical inhomogeneities are well-documented issues in single crystal growth techniques where the chemical composition of the grown crystal differs from the stoichiometric composition due to either the loss of a volatile component at high temperatures during crystal growth [23], differences in the segregation coefficients of the components/elements, or due to the shifts of the congruently melting composition towards compositions richer in rare earth [24]. However, it will be shown later in **section 1.7** from the magnetic susceptibility measurements that the crystal grown has the same glass transition temperature as the polycrystalline sample of composition $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$. This is the reason why the $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ composition will be taken in this manuscript as the real composition of the crystal grown.

1.4 XANES analysis

Given the determined A-site composition as $\text{Ba}_{0.8}/\text{La}_{1.2}$, it is critical to determine the oxidation state of Mn. There are two possibilities, mixed 20% Mn^{2+} / 80% Mn^{3+} at the Mn site or 10% excess of O^{2-} for which there is only Mn^{3+} on the B-site.

To clarify the average oxidation state of Mn in $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ (both single crystal and polycrystalline), Mn-edge XANES analysis was employed. The normalized XANES spectra of the samples are plotted in **Figure 2**, together with a selected set of XANES spectra of reference Mn compounds with different Mn valence states and the same manganese ligands (oxygen atoms) as in the investigated samples (Mn^{2+}O , Mn^{3+}_2O , Mn^{4+}O_2 , $\text{BaLaMn}^{3+}\text{O}_4$, and $\text{Ba}_{0.8}\text{La}_{1.2}\text{Mn}^{3+\delta}\text{O}_{4+\delta}$). The valence state of Mn cation in the analysed samples can be deduced from the energy shift of the Mn absorption edge. With increasing the oxidation state, the Mn absorption edge is shifted to higher energies for about 3.5 eV per unit oxidation state between Mn^{2+} and Mn^{4+} , as observed on reference Mn compounds (**Figure 2**) and in agreement with previous observations [25,26].

From the XANES analysis, **Figure 2**, we can see that the Mn K-edge position in the $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ coincides with the Mn K-edge position for BaLaMnO_4 and the Mn K-edge position in Mn_2O_3 reference compound (indicated in **Figure 2** by a vertical line positioned at the energy of the absorption edge of Mn_2O_3). On the other side, for $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4+\delta}$ (sample obtained by oxidizing the $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ in air) the Mn K-edge position is shifted to higher energies by about 0.7 eV indicating an average valence state of about +3.4(1).

Figure 2 Mn K-edge XANES spectra of the $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ (crystal and polycrystalline), BaLaMnO_4 and reference Mn compounds with different Mn valence states between (Mn^{2+}O , $\text{Mn}_2^{3+}\text{O}_3$, BaLaMnO_4 , and Mn^{4+}O_2). The vertical dotted line is positioned at the energy of the absorption edge of Mn_2O_3 at 6550 eV.

Therefore, the Mn K-edge XANES measurements indicate that Mn in $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ (both single crystal and polycrystalline) is in a +3.0(1) oxidation state only. Any admixture of Mn^{2+} can be ruled out. This implies that for charge balance, $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ has to contain an

excess of oxygen. This oxygen can be accommodated as interstitial oxygen defect and neutron powder diffraction is a good technique to probe that.

1.5 TOF Neutron Diffraction

A_2BO_4 oxides with the K_2NiF_4 -type structure have been known to poses sufficient space to allow extra oxygen to be incorporated at interstitial species [27, 28, 29]. In this type of compounds, the interstitial oxygen has been found from neutron powder data to be located at (0.25, 0.25, 0.25) site in an orthorhombic structure [28] which is equivalent to (0.5, 0, 0.25) in an undistorted $I4/mmm$ structure [29]. This site is situated in the rock salt layer where there is more than enough space available to accommodate the extra oxygen ions [27]. Indeed, in a previous report [15], the excess O^{2-} was found to be located in $Sr_{0.8}La_{1.2}MnO_{4.27}$ at Wyckoff site 4d (0.0 0.5 0.25) of the $I4/mmm$ space group.

An attempt to locate the extra O^{2-} in our sample was carried out using the TOF data from NOMAD, see **Figure 3**. The measurement was performed on a crushed single crystal with the $Ba_{0.8}La_{1.2}MnO_{4.1}$ composition. These data were truncated at $Q = 14 \text{ \AA}^{-1}$ corresponding to a $d_{\min} = 0.449 \text{ \AA}$. During the refinement, the La:Ba ratio, the site occupancy of the interstitial oxygen together with their thermal parameters were allowed to vary. The occupancies of Mn, O1 and O2 were constrained to the nominal values.

Figure 3 Refinement of the NOMAD data for $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ powder at 295 K. The difference plot shows the quality of the fit and the vertical bars represent the Bragg peak positions. Rietveld refinement of the neutron TOF data collected at NOMAD provides evidence for this choice and located the extra oxygen at (0.5, 0, 0.25) position **Figure 4**. **Table 1** presents the structural parameters from the fits and shows that $\delta = 0.082(16)$ which leads to the following chemical formula: $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$.

Figure 4 The $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ unit cell at 295 K highlighting the location / environment of the interstitial oxygen defect which is located in the perovskite / rock salt intergrowth region.

Table 1 Results of the Rietveld refinements of the neutron diffraction data for $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ in space group $I4/mmm$ with the excess O^{2-} in 4d ($\frac{1}{2}$ 0 $\frac{1}{4}$). $R_{\text{wp}} = 3.56\%$. The $a = 3.88812(11)$ Å, $c = 13.29856(71)$ Å, $V = 201.041(11)$ Å³.

Atom	Wyckoff positions	x	y	z	U	Occupancy
La	4e	0.5	0.5	0.85792(15)	0.020(4)	0.62(4)
Ba	4e	0.5	0.5	0.85792(15)	0.019(10)	0.38(4)
Mn	2a	0.5	0.5	0.5	0.0165(6)	1 [#]
O ₁	4e	0.5	0.5	0.67342(13)	0.0732(3)	1 [#]
O ₂	4c	0.5	0	0.5	0.0034(6)	1 [#]
O _{int}	4d	0.5	0	0.25	0.064(6)	0.041(16)

[#]this parameter was kept fixed during the refinement.

The above results support strongly the composition $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ which is consistent with only Mn^{3+} present and are completely in accord with the XANES spectra. In addition, the unit cell parameters obtained on the crushed crystal at 295 K match well those obtained on the polycrystalline powder with the $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ composition (see **SI Table 3**) which further support the stoichiometry of the crystal.

1.6 Local structure from Neutron Pair Distribution Function (NPDF)

The NOMAD data were also analysed using NPDF techniques to examine the local structure, especially to address the issue of Ba/La site ordering. As the La^{3+} and Ba^{2+} cations have much different ionic radii (1.16 Å vs. 1.42 Å) it can be expected that local distortions must be present to accommodate this size difference. The pair distribution function (PDF) provides information on the actual bond distribution for each cation and was used to explore the local structure. Both small box PDFgui and large box Reverse Monte Carlo (RMC) were applied.

A fit of the PDF using the average structure - **SI Figure 3** was able to generally produce the observed features, although there were regions that were poorly fit, R_w is somewhat large, 17.8%. Not surprisingly, one of the worst fit regions was the second peak corresponding to Ba–O, La–O, and O–O distances, which has a more complex shape than can be accounted for by the *I4/mmm* structure. The resulting positional and displacement parameters are displayed in **SI Table 2**. It can be seen that they agree well with those from the Rietveld fit displayed in **Table 3** above. Thus, the local structure did not deviate strongly from the average structure.

A first consideration was to clarify if any short range ordering of the Ba and La was occurring to reduce the strain. Three ordered models were generated which had different patterns of layering for these cations – **SI Figure 4** and their effect on bond stability and local structure was analysed. Fitting with these models did not improve the fits and the extra degrees of freedom tended to refine to values very close to the fixed values of the *I4/mmm* model, which seems to indicate that the Ba/La distribution is completely random even over a short length scale.

To model the PDF, the Reverse Monte Carlo (RMC) method was employed. A $15 \times 15 \times 6$ supercell of the crystal structure was used which had a single interstitial oxygen in one out of every 5 unit cells, giving a 2.5% excess of O and 19,170 total atoms in the model. Since the PDFgui refinements did not indicate any ordering on the A-site, for the RMC fits the Ba and La distribution was randomized by swapping these atoms prior to refining against the data. As the RMC method could be expected to do a good job determining the A–O distribution but a poor job at separating out the Ba–O and La–O distributions, bond valence constraints were used for all ions to produce a solution that both fit the experimental $G(r)$ and was energetically plausible. The RMC refinement was able to produce an excellent fit to the $G(r)$ while also having average BVS values for all ions that were within a few percent of the ideal values. This demonstrates that for this structure it is possible to accommodate the size differences of Ba and La by local displacements of these cations and the surrounding oxygen atoms even when the distribution is random.

RMC calculations were also carried out after adding interstitial oxygen into the configuration. However, the results were essentially the same, the additional oxygen did not seem to impact the refinement. This was not a surprising result considering the amount.

The actual bond distances can be obtained from the atom-atom distance distribution, partial $G(r)$ of the final RMC configuration – **Figure 5b, c**. The Mn–O distribution, **5b**, shows the two distances resulting from the Jahn-Teller distortion which agree well with the Rietveld results, SI Table 3. The partial $G(r)$ for the La–O and Ba–O pairs are shown in **Figure 5c**. At the nearest neighbour positions, the two bonds are unsurprisingly distinguishable, the average La–O bond is found to be 2.64 Å, much shorter than the average Ba–O bond of 2.81 Å. This difference disappears by the third neighbour position, indicating only a very short range La/Ba ordering.

Figure 5 The RMC fit for $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ for a wide r -range (a). The black circles represent the experimental data while the red line is the RMC fit. The Mn–O (b) and La–O plus Ba–O (c) bond distributions obtained from RMC modelling.

The Mn–O–Mn bond angle distribution, $f(\theta)$, and $f(\theta)/\sin(\theta)$ are shown in **SI Figure 5**. While the $f(\theta)/\sin(\theta)$ curve shows that the distribution is centred around 180° , the distribution is much broader than is normally observed [30,31]. Such a broad distribution is unlikely due to thermal vibrations alone and is caused by local oxygen displacements, the direction and magnitude of which depends on the local configuration of La/Ba ions around that oxygen. As Mn–O–Mn pathways are responsible for super-exchange this angle distribution is directly relevant for understanding the magnetism. The large variation in angles could contribute to a weakening of the AF exchange and a strengthening of the F interactions. While the Mn–O–Mn angle distribution in $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ has not been experimentally determined it is likely much narrower as Sr^{2+} and La^{3+} are more similar in size and this difference in angle distribution width may contribute to the differences in magnetic properties despite the average Mn–O–Mn angle being 180° in both cases.

1.7 Magnetic properties (dc and ac susceptibility)

Magnetic susceptibility data for $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ were obtained on both powders and single crystals. In order to study the low temperature magnetic properties, we measured the dc magnetisation of $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ down to 2 K. For the polycrystalline samples, a field of 100 Oe was applied. For the single crystal measurements, the same magnetic field of 100 Oe was applied orthogonal to and parallel to the c -axis (the longest axis).

As shown in **Figure 6a** and **6b**, the magnetic properties are highly anisotropic. The $H \parallel c$ data exhibits a broad peak centred at 26.4(4) K with a ZFC-FC divergence (inset **Figure 6a**) at the same position, behaviour which is consistent with a spin glass transition (with $T_g = 26.4(4)$ K). On the other hand, the magnetic susceptibility for $H \perp c$ exhibits a quasi-paramagnetic behaviour, **6b**, down to 2 K. Inset in **Figure 6b** also shows that the T_g of polycrystalline sample is located at 26.6(4) K, same as for the crystal with $H \parallel c$. **Figure 6c** shows a simulation of the expected polycrystalline data obtained as $\chi_{\text{(powder)}} = 1/3 \cdot \chi \parallel c + 2/3 \cdot \chi \perp c$. This is compared with the data for a crushed crystal, **Figure 6d**, and the agreement is excellent. Note the unusual shape of the ZFC curve for the powder data (insets **Figure 6c, 6d**) which shows a peak at T_g followed by an upturn and a broad maximum at lower temperatures, which is in sharp contrast to that for an isotropic spin glass for which the ZFC data fall rapidly below T_g . This suggests that $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ is a new example of an exceedingly rare class of materials which show anisotropic spin glass behaviour. That is, only one spin component freezes below T_g while the other two remain more or less dynamic. Previously, the only other known insulating anisotropic

spin glass was Fe_2TiO_5 [32]. It should also be noted that polycrystalline BaLaMnO_4 shows the same magnetic susceptibility behaviour with $T_g = 19(1)$ K, as reported earlier, and thus presents an additional example.

Figure 6 Magnetic susceptibility for $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$; **(a)** Single crystal with $H \parallel c$ showing a clear spin glass transition at $T_g = 26.2(2)$ K (inset); **(b)** Single crystal with $H \perp c$ showing no transition and the inset showing the T_g of the polycrystalline sample **(c)** Simulated for a powder sample by combining data from **(a)** and **(b)**. **(d)** Data for a powder sample (crushed single crystal). Note the unusual shape of the ZFC curve(insets) in **(c)** and **(d)**.

In SI Figure 6 are shown Curie-Weiss fits for both field orientations. Fitting data for $T > 225$ K yielded the Curie-Weiss temperature of $\theta_{\text{cw}} = -1.6(2)$ K for the $H \parallel c$, and $-3.6(3)$ K for the $H \perp c$ axis, respectively, very small values in comparison with T_g , consistent with the presence of competing and nearly equal ferro- and anti-ferromagnetic exchange which could explain the spin glass ground state. The Curie constants are $+4.0144(8)$ for the $H \parallel c$ and $+4.0171(5)$ emu K mol^{-1} for the $H \perp c$ axis, respectively, values equivalent to an effective magnetic moment of $5.66(1) \mu_B$, which is larger than the spin only value contribution of Mn^{3+}

of $4.90 \mu_B$. The XANES results and the TOF neutron diffraction data have already ruled out the presence of Mn^{2+} as an explanation for the large effective moments. For example, one would require 72% Mn^{2+} to reach the observed values. At this time the origin of this discrepancy is unclear.

To confirm the spin glass behaviour *ac* susceptibility measurements were carried out with the results shown in **Figure 7**. No maximum was observed with $H \perp c$. But with $H \parallel c$ a frequency-dependent maximum is observed in χ' (top). From the Mydosh parameter (**Equation 4**):

$$k = \Delta T_f / [T_f \cdot \Delta(\log \omega)] \quad (4)$$

a value of 0.0357 is obtained which falls well within the range for spin-glasses (0.004–0.08) [33]. While the χ'' data, (**Figure 7** bottom) are noisy, the expected sharp decrease above T_g characteristic for a spin glass material [33] is observed along with a frequency dependence. The weak χ'' values are likely due to the fact that only one of three spin components freeze.

Figure 7 The temperature dependence of the real part (top) and imaginary part (bottom) of the ac magnetic susceptibility of $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$. Note the shift in the position of χ' and χ'' (max) with increasing frequency.

1.8 Heat Capacity

Heat capacity data on the $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ single crystal is shown in **Figure 8 a–d**. Clearly, in **Figure 8a**, there is no evidence of long range magnetic ordering as indicated by the absence of a characteristic λ -type peak, consistent with the spin glass ground state. The total heat capacity has both electronic and phonon (lattice) contributions. Therefore, in order to estimate the lattice component, the heat capacity of a diamagnetic isostructural compound, SrLaGaO_4 [34,35] was also measured. This material was chosen as it crystallises in the same structure-type and the electronic configuration of Ga is $[\text{Ar}]\text{3d}^{10}$ so there are no unpaired electrons in the outer shell to contribute in the heat capacity. Also, the close proximity of Ga to Mn in the periodic table minimizes the mass difference. A strong Jahn-Teller effect is expected in the $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ compound due to the Mn^{3+} (d^4) ion with an odd number of electrons present in the e_g orbital.

The system is reducing its energy by lifting the degeneracy of the e_g orbitals. This leads to the deformation of the MnO_6 octahedra resulting in 4 short (1.9497(10) Å) and 2 long (2.282(3) Å) Mn–O bonds. However, Ga^{3+} is not a Jahn Teller ion since it has a d^{10} configuration with fully occupied d orbitals. Therefore, the GaO_6 octahedron is not experiencing a static Jahn-Teller distortion. However, due to the mismatch between the perovskite and rock-salt layer of the K_2NiF_4 -type structure, the GaO_6 octahedron experience a small elongation along the [001] direction leading to 2 long Ga–O (2.122(3) Å) and 4 short Ga–O (1.9218(2) Å) bonds [35].

During the heat capacity analysis, it was necessary to scale the SrLaGaO_4 data to equal the sample heat capacity of at 120 K, the maximum measurement temperature. By subtracting this estimated phonon contribution from the total specific heat, an estimate of the magnetic contribution was obtained, **Figure 8b**. Note that at low temperatures, below about 12 K, the magnetic heat capacity follows a T^1 power law, consistent with a spin glass ground state. Also the broad maximum in the magnetic heat capacity (**Figure 8b**) occurs near 40 K, somewhat higher than $T_g = 26$ K, also consistent with spin glass behaviour. From **Figure 8c** the entropy loss, ΔS , can be estimated, **Figure 8d**. Over the range 2K – 75K the $\Delta S = 8.75$ e.u. which is 65% or the theoretical total, $R \ln(2S+1)$, of 13.37 e.u., where R is the gas constant and $S = 2$. For the range 2K – 26.5K (T_g) $\Delta S = 3.33$ e.u. or 38% of the observed loss and 25% of the theoretical total.

Figure 8 (a) The heat capacity measured on a $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ single crystal in zero applied field and the lattice match SrLaGaO_4 . As described in the text, the SrLaGaO_4 data were scaled to equal the $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ data at 120 K. (b) The magnetic heat capacity, C_{mag} , obtained by subtraction of the scaled lattice match data and (c) C_{mag}/T versus T from which the magnetic entropy was calculated. Entropy loss, ΔS , values for selected temperature ranges are shown. (d) Temperature dependence of the magnetic entropy.

1.9 Magnetic neutron powder diffraction – C2

For spin glasses no magnetic Bragg peaks should be seen in a neutron diffraction pattern. From the neutron powder diffraction measurements performed on the polycrystalline $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$, at temperatures below and above the glass transition $T_g = 26$ K, no magnetic Bragg peaks or magnetic diffuse scattering were observed. **Figure 9** shows the 35 and 3.5 K neutron diffraction patterns together with the difference intensity – **Figure 9c**. From **Figure 9c** it can be clearly seen that there is no sign of long-range ordering in the difference plot. Peak positions for the expected $\mathbf{k} = (\frac{1}{2} \frac{1}{2} 0)$ magnetic structure observed for SrLaMnO_4 and many other K_2NiF_4 structure materials are indicated.

Figure 9 (a) Neutron powder diffraction patterns of $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ obtained at 3.5 K (base temperature), and 35 K (above T_g) (b) The difference in intensities between the neutron diffraction patterns obtained at 3.5 and 35 K for $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$. No magnetic peaks were observed. The green arrows indicate the expected positions of the magnetic peaks assuming an antiferromagnetic structure as for SrLaMnO_4 .

The C2 data at 295 K, 35 K and 3.5 K were refined on the same model as used for the NOMAD data and the results are displayed in **SI Table 3**. Note that the distortion index, $D.I.$, defined as:

$$D.I. = [(B - O)_{\text{axial}} - (B - O)_{\text{planar}}] / \langle B - O \rangle \quad (5)$$

does not vary with temperature and that the BVS are consistent with $\text{Ba}^{2+}/\text{La}^{3+}$ on the A-site and Mn^{3+} on the B-site.

In summary the characterization of $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ as a K_2NiF_4 structure oxide containing only Mn^{3+} and which exhibits a very rare anisotropic spin glass ground state is

robust. The contrast with isostructural $\text{Sr}_{1.2}\text{La}_{0.8}\text{MnO}_4$ with mixed $\text{Mn}^{4+}/\text{Mn}^{3+}$ on the B-site, an isotropic spin glass, is interesting and remarkable.

2 $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4+\delta}$

2.1 Mn K-edge XANES analysis

As for $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$, the Mn K-edge XANES analysis was used to obtain information about the average oxidation state of Mn in polycrystalline $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$. The XANES analysis revealed that Mn K-edge position in the $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ coincides with the Mn K-edge position for $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$, BaLaMnO_4 , and the Mn K-edge position in Mn_2O_3 reference compound (indicated in **Figure 10** by a vertical line positioned at the energy of the absorption edge of Mn_2O_3 at 6550 eV).

Figure 10 Mn K-edge XANES spectra of the $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$, $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ and reference Mn compounds with different Mn valence states between Mn^{2+} (MnO), Mn^{3+} (Mn_2O_3) and Mn^{4+} (MnO_2). The vertical dotted line is positioned at the energy of the absorption edge of Mn_2O_3 at 6550 eV.

The Mn K-edge XANES measurements indicate that Mn in the $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ compound is in a +3.0(1) oxidation state only and, for charge balance this implies that $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4+\delta}$ has to contain an excess of oxygen, $\delta = 0.1$, and not mixed $\text{Mn}^{2+}/\text{Mn}^{3+}$ valence on the Mn site. These results are similar to the Ba analogue.

2.2 Crystal structure

As for $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4+\delta}$, the $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4+\delta}$ phase also adopts the tetragonal structure with the $I4/mmm$ space group, which was confirmed with both laboratory X-ray and neutron powder diffraction. The unit cell constants and the overall results from the refinements of the data collected at several temperatures are shown in **SI Table 4**. Note that the distortion index is larger for the Sr-based oxide and that, again, the BVS agree with the A and B site occupations with only Mn^{3+} on the B-site. Attempts were made to locate the extra 10% of O^{2-} but these were not successful, likely due to the limited Q-range of the C2 data, $Q_{\text{max}} \sim 8 \text{ \AA}^{-1}$ relative to $Q_{\text{max}} > 14 \text{ \AA}^{-1}$ for the NOMAD data.

2.3 Magnetic properties

The temperature-dependent magnetic susceptibility data of $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ are presented in **Figure 11a**. $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ shows a broad maximum in the dc magnetic susceptibility, near 125 K, characteristic of strong intra planar 2D antiferromagnetic correlations. The Fisher heat capacity [36] was obtained using the magnetic susceptibility data. For this analysis, the derivative of the χT to $T/(d(\chi T)/dT)$ plotted versus T gives a good approximation to the magnetic component of the heat capacity. The Fisher capacity analysis indicated a T_N of about 94(1) K – **Figure 11b**.

The $1/\chi$ versus temperature is plotted in **Figure 11c**, while **Figure 11d** shows the C-W fit for the high temperature range. Several temperature ranges were selected for the fit and the C-W parameters derived from these fits showed a very strong dependence on the temperature range chosen (see **SI Table 5**). Therefore, some caution should be taken when interpreting the results of the fits. We chose $\theta = 31$ K because this value did not change much as a function of the fitting range. Given the presence of competing F and AF interactions and the 2D magnetism, it is not impossible for the net exchange to be slightly positive while the overall net is AF. $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ is an unusual AF material in terms of the small ordered moment, $1.3 \mu_B$ and there is much which is not understood.

Figure 11 (a) Field cooled and zero field cooled magnetic susceptibility data for polycrystalline $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ (b) first derivative, $d\chi/dT$ Fisher heat capacity indicating a T_N of about 94(1) K. (c) $1/\chi$ versus temperature where the three regimes are marked: **I** is the 3D antiferromagnetically ordered state, **II** represents the two-dimensional magnetic correlations, and **III** represents the onset of the paramagnetic state (d) Curie-Weiss fit to the paramagnetic region for a range of temperatures between 300 K and 700 K.

A value for the intra planar exchange, J/k_B , can be estimated from **Equation 6** below, where $\tau_m = 2.71$ appropriate for a square lattice $S = 2$ system, to be = 7.8 K [37].

$$\tau_m = k_B T_{max} / |J|S(S + 1) \quad (6)$$

Li et al. [15] have reported similar values for T_N for an-oxygen deficient version with the chemical formula: $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{3.94}$. The magnetic susceptibility of this “reduced” phase shows a similar broad maximum located around 110 K (also an indication of the 2D antiferromagnetic correlations) and a T_N of about 80 K. Their result is somewhat surprising for a reduced phase which contains $\text{Mn}^{2+}/\text{Mn}^{3+}$ ions as they would give FM interactions through

the $\text{Mn}^{2+} (d_{x^2} - d_{y^2})^1 - \text{O } 2p - \text{Mn}^{3+} (d_{x^2} - d_{y^2})^0$ superexchange and double-exchange interactions.

The field dependence of the susceptibility shown in **SI Figure 7** did not show any hysteresis which is in accordance with the value of the frustration index and the absence of a ferromagnetic response in the magnetic susceptibility data.

2.4 Neutron powder diffraction / Magnetic structure

Neutron powder diffraction data were collected for temperatures between 290 and 6 K in order to understand the temperature dependence of the magnetic ordering in this material. **Figure 12** shows the temperature dependent neutron diffraction patterns for polycrystalline $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$.

At 290 K there was no indication of any short or long range magnetic order in this material, only the structural Bragg peaks are observed. At temperatures between 100–95 K broad features/peaks are observed. These are highly asymmetrical, typical of the Warren lineshape, indicative of 2D spin correlations [38]. At 95 K and below, additional Bragg reflections of magnetic origin are clearly visible which is consistent with $T_N = 94(1)$ K as determined from the Fisher heat capacity [36]. The low temperature data sets were refined using 15 parameters including an additional magnetic phase. The magnetic structure is the $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, 0)$ type typical for such materials with the Mn^{3+} moment along the c -axis. The magnetic phase (95 K) has a unit cell of $a = b = 5.4070(7)$ Å, $c = 13.0480(7)$, $V = 381.47(7)$ Å³.

Figure 12 Neutron diffraction patterns ($\lambda = 1.33 \text{ \AA}$) for $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ collected at selected temperatures between 6 and 290 K. The indicated magnetic structure peaks are indexed on the magnetic unit cell where $a_{\text{mag}} = \sqrt{2} \cdot a_{\text{cryst}}$.

SI Table 4 presents the agreement factors Rietveld refinement of the neutron powder diffraction data for the crystallographic and magnetic phases of $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ plus the magnetic moment. **Figure 13** shows the evolution of the refined Mn^{3+} moment as a function of temperature. The disappearance of the Bragg peaks above 95 K is in agreement with the Néel temperature determined from the Fisher heat capacity, $T_N = 94(1) \text{ K}$. From **SI Table 6** can be seen that the refined moment on Mn^{3+} is $1.449(49) \mu_B$, a value which is significantly lower than the expected $S = 2$ spin-only value for Mn^{3+} of $4.0 \mu_B$ or even $3.3 \mu_B$ observed for SrLaMnO_4 . This is quite remarkable as the paramagnetic moment is close to that expected for $S = 2$. (**Figure 11**).

Figure 13 Temperature dependence of the refined Mn^{3+} moment versus temperature for $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$. The inset shows the evolution of the Gaussian width of the (101) magnetic reflection. Note significant broadening above 90 K.

Conclusions

Two K_2NiF_4 structure oxides, $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ and $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$, have been synthesized, the former as a single crystal, and their magnetic properties have been studied in detail. Both are shown to contain Mn^{3+} only requiring interstitial O^{2-} for charge balance, which has been observed directly for the Ba-phase. The magnetic properties are strikingly different. $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ is a rare example of an anisotropic spin glass, in which spin freezing occurs only with the applied field along the c -axis, $T_g = 26.4$ K, while the spin components normal to c -axis remain more or less paramagnetic below T_g . On the other hand, $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ is a more conventional 2D antiferromagnet with $T_N = 95(1)$ K and evidence for short range 2D spin correlations in both the dc susceptibility and neutron diffraction. However, the ordered Mn^{3+}

moment of $1.449(49) \mu_B$ is anomalously small relative that expected for $S = 2$ ($4.0 \mu_B$) and that observed for SrLaMnO_4 ($3.3 \mu_B$) [8,9].

Our observations agree well to the results of a polarized neutrons study that was recently reported in Ref. [10], in which BaLaMnO_4 (studied as a part of the system $\text{Ba}_x\text{Sr}_{1-x}\text{LaMnO}_4$) was shown to exhibit no spin-spin correlations and to undergo an apparent spin freezing transition below, $T_g = 19.2\text{K}$ [10]. In fact, the data presented here for $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$ seem to also establish the anisotropic spin glass ground state for BaLaMnO_4 . In Ref. [10], SrLaMnO_4 and phases up to $x = 0.25$ show long range AF order and 2D spin correlations. In the case of $x = 0.25$, the ordered moment on Mn^{3+} is actually $1.1 \mu_B$, again far smaller than that for SrLaMnO_4 . In this case a quite remarkable magnetic phase separation was observed, i.e., the magnetic scattering was partitioned between a Bragg component and a diffuse component, resulting in the much reduced ordered Mn^{3+} moment. It is likely that a similar phenomenon is responsible for the reduced Mn^{3+} moment for $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_4$ but this has not been verified to date.

Finally, what is responsible for the spin glass state for $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$? Again, in the recent polarized neutron study, a mechanism was proposed to explain the differences between the magnetic ground states of SrLaMnO_4 and BaLaMnO_4 [10]. This explanation relies on the existence of competing AF and F 180° superexchange interactions for the Mn–O–Mn nearest neighbour exchange, see **SI Figure 4**. The substitution of the larger Ba^{2+} for Sr^{2+} induces subtle changes in the Mn–O bond lengths, among them the reduction in the distortion index for the Mn–O octahedron and an increase in the n.n. Mn–O distances. It is argued that the former change strengthens the F pathway while the latter weakens the AF pathway, resulting in a near cancellation which allows the existence of the glassy ground state for BaLaMnO_4 . Similar structural changes are seen between $\text{Sr}_{0.8}\text{La}_{1.2}\text{MnO}_4$ and $\text{Ba}_{0.8}\text{La}_{1.2}\text{MnO}_{4.1}$, **SI Tables 3 and 4**.

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