Large effects of A-site average cation size on the properties of the double perovskites
\( \text{Ba}_{2-x}\text{Sr}_x\text{MnReO}_6 \): A \( d^5-d^1 \) system

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\( \text{Ba}_{2-x}\text{Sr}_x\text{MnReO}_6 \) (\( x = 0, 0.5, 1, 2 \)) phases with a double-perovskite structure were prepared by solid-state techniques in evacuated sealed silica tubes. Mn\(^{2+}\) and Re\(^{6+}\) are virtually completely ordered on the \( B \) sites. The compounds are ferrimagnetic below 120 K. The maximum saturation moment was obtained for a compound with \( x = 0.5 \) whose tolerance factor is closest to 1. The whole series of compounds, \( 0.0 \leq x \leq 2.0 \), exhibits semiconducting behavior with variable-range hopping type of conduction. \( \text{Sr}_2\text{MnReO}_6 \) has an unusually high coercive field \((2.6 \text{ T at } 5 \text{ K})\) and two transitions in the \( M-H \) loop. \( \text{Ba}_2\text{MnReO}_6 \) shows large positive magnetoresistance \((14\% \text{ at } 80 \text{ K}, 5 \text{ T}) \) below 140 K, while the other compositions studied exhibit negative magnetoresistance in the temperature range measured.

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I. INTRODUCTION

The recent discovery of large low-field room-temperature magnetoresistance in the double perovskite \( \text{Sr}_2\text{FeMoO}_6 \) (Ref. 1) sparked interest in ferrimagnetic double perovskites.\(^2\)-\(^6\) The structure of \( \text{A}_2\text{B}'\text{B}''\text{O}_6 \) double perovskites is similar to that of simple perovskites, \( \text{ABO}_3 \), except that the \( \text{B}' \) and \( \text{B}'' \) ions can order with a concomitant doubling of the unit cell; the ordered structure is manifested by the appearance of superstructure peaks in the powder x-ray diffraction (PXD) pattern.

In the ferrimagnetic state in these materials alternating paramagnetic \( \text{B}' \) and \( \text{B}'' \) ions form two interconnecting sublattices, each with ferromagnetic (FM) order but in an antiparallel alignment with respect to each other. The larger the difference in the number of unpaired electrons on the \( \text{B}' \) and \( \text{B}'' \) ions, the larger the net magnetic moment that results. The highest moment that can be obtained in double-perovskite ferrimagnets with six-coordinated paramagnetic ions is \( 4 \mu_B \). For example, in \( \text{Sr}_2\text{FeMoO}_6 \), \( \text{Fe}^{3+} \) is \( d^5 \) high spin and \( \text{Mo}^{5+} \) is \( d^1 \) (Refs. 7 and 8; also the \( \text{Fe}^{3+}/\text{Mo}^{5+} \sim \text{Fe}^{2+}/\text{Mo}^{6+} \) distribution is reported, for example, in Refs. 9 and 10).

The structural “perfection” of simple perovskite \( \text{ABO}_3 \) can be described by the tolerance factor \( (t) \),\(^11\) with

\[
t = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}},
\]

where \( r_A, r_B, \) and \( r_O \) are the ionic radii of \( \text{A}, \text{B}, \) and \( \text{O} \), and oxygen and \( t = 1 \) corresponds to an ideal cube. Thus the tolerance factor is a semi-quantitative estimate of how close an \( \text{ABO}_3 \) perovskite is to the cubic structure; moreover, for a large deviation of \( t \) from 1 the perovskite structure is likely to be unstable. It was shown that perovskites \( \text{ABO}_3 \) (e.g., \( \text{B} = \text{Mn} \)) exhibit enhanced electronic and magnetic properties if their tolerance factors are close to 1 (Ref. 12).

The tolerance factor concept can be adapted to double perovskites as well. In general, for double perovskites, with mixed \( A \)-site \( A'_1-A''_1 A'_2-B'_2 B''_2 O_6 \) or \( (A'_1-A''_1 A'_2) B'_2 B''_2 O_6 \), the tolerance factor can be written as

\[
t = \frac{1 - \frac{x}{2} r_{A'} + \frac{x}{2} r_{A''} + r_O}{\sqrt{2\left(\frac{r_{B'}^2}{2} + \frac{r_{B''}^2}{2} + r_O^2\right)}},
\]

where \( r_{A'}, r_{A''}, r_{B'}, \) and \( r_{B''} \) are the ionic radii of the respective ions.

It is worth noting that based on the ionic radii reported by Shannon,\(^13\) the calculated \( t \) of \( \text{Sr}_2\text{FeMoO}_6 \) is 0.990, i.e., very close to 1. Substitution at the \( A \) site, to bring the tolerance factor closer to 1, enhances the low-field room-temperature magnetoresistance of \( \text{Sr}_2\text{FeMoO}_6 \) (Ref. 14), which could lead to potential applications of this material.

If \( \text{Mn} \) is \( 2 + (d^5) \) and \( \text{Re} \) is \( 6 + (d^1) \), \( \text{A}_2\text{MnReO}_6 \) (\( A = \text{divalent cation} \) double perovskite would be iso-electronic with \( \text{Sr}_2\text{FeMoO}_6 \). Moreover, the composition where \( A \) is \( 36\% \) \( \text{Sr} \) and \( 64\% \) \( \text{Ba} \) would have the tolerance factor equal to 1. This prompted us to investigate the title compositions. \( \text{Ba}_2\text{MnReO}_6 \) was first synthesized in 1961 by Longo and Ward.\(^15\) Initially, Sleight et al.\(^16\) suggested that the oxidation state of \( \text{Mn} \) is \( 3+ \) and that of \( \text{Re} \) is \( 5+ \), based on their finding that the saturation moment of \( \text{Ba}_2\text{MnReO}_6 \) was \( M_s = 0.58 \mu_B \). Subsequently Sleight and Weiher\(^17\) reported a saturation moment of \( 3.91 \mu_B \) and ferrimagnetic ordering at the Néel temperature \( (T_N) \) of 105 K for this phase. They also confirmed that \( \text{Ba}_2\text{MnReO}_6 \) was cubic\(^17\) and proposed \( \text{Mn}^{2+} \) and \( \text{Re}^{6+} \) as the most probable oxidation states of the ions consistent with their data. In 1975 Khatkatt et al.\(^18\) confirmed the complete ordering of \( \text{Mn}^{2+} (d^5) \) and \( \text{Re}^{6+} (d^1) \) ions, as well as a transition to the ferrimagnetically ordered state below \( 105 \text{ K} \), by neutron diffraction analysis. \( \text{Ba}_2\text{MnReO}_6 \) has not been revisited ever since and \( \text{Sr}_2\text{MnReO}_6 \) has never been reported.

In this paper we report the synthesis and characterizations of the \( \text{Ba}_{2-x}\text{Sr}_x\text{MnReO}_6 \) series of compounds with particular...
focus on the effect of the variation of $t$ with $x$ on the physical properties. The tolerance factor ranges from $1.0183 \geq t \geq 0.9609$ for $0.0 \leq x \leq 2.0$, and $t = 1$ is predicted for $x = 0.72$ [Eq. (2)].

II. EXPERIMENT

The $\text{Ba}_2\text{Sr}_x\text{MnReO}_6$ compounds were synthesized from $\text{BaO}$, $\text{SrO}$, $\text{MnO}$, and $\text{ReO}_3$. $\text{BaO}$ was prepared by decomposition of $\text{BaCO}_3$ (Aldrich, A.C.S. reagent, 99+%) in dynamic vacuum first at 950 °C for 1 h, then at 1100 °C for 3 h. $\text{SrO}$ was prepared by decomposition of $\text{SrCO}_3$ (Aldrich, 99.9%) in air at 1400 °C for 5 h. $\text{MnO}$ was prepared by reduction of finely ground $\text{Mn}_2\text{O}_3$ (Fisher, 99.6%) under 10%-H$_2$/90%-N$_2$ flow at 850°C for 20 h. All compounds upon removal from the furnace were immediately placed into a dry box. $\text{ReO}_3$ was used as purchased (Aldrich, 99.9%).

The method of $\text{Ba}_2\text{MnReO}_6$ synthesis described in Ref. 15, where the authors sintered stoichiometric mixtures of oxides at 1000°C in evacuated silica tubes for 24 h, did not lead to single phase compounds. Also a reaction between the silica tube and the pellet was observed.

In order to obtain single phases, mixtures of ground and pelletized starting materials in stoichiometric proportions were wrapped into a platinum foil and sealed in evacuated silica tubes. Care was taken not to overheat the samples while sealing the silica tubes under vacuum, because of the high vapor pressure of $\text{ReO}_3$ at relatively low temperatures. Samples were sintered for a total of 170 h at 1000°C with two intermediate grindings and finally cooled down slowly in the furnace. Powder x-ray diffraction analysis showed that the products were single-phase compounds.

PXD data for Rietveld analysis were obtained with a Scintag PAD V diffractometer (CuKα radiation) in the range of 10–120° 2θ with a step size of 0.02° and collection time of 8 sec at each step. The PXD patterns were analyzed using the GSAS program with EXPGUI shell. Magnetic measurements were performed with a Quantum Design superconducting quantum interference device (SQUID) magnetometer (MPMS-XL). Magnetoresistance measurements were performed on the same instrument using External Device Control and Keithley equipment by the standard four-probe technique. Temperature-dependent resistivity measurements were carried out on a Displex by four-probe technique.

The x-ray absorption spectroscopy (XAS) measurements were carried out on beamlines X19A (for Mn) and X18B (for Re) with double-crystal and channel-cut Si-111 monochromators, respectively. Both transmission and fluorescence mode measurements were collected for the samples. Simultaneous standards were run with the samples for precise energy calibration. The XAS spectra were normalized to unity absorption step height well above the edge after a linear background subtraction.

III. RESULTS AND DISCUSSION

According to x-ray powder diffraction data all of the $\text{Ba}_2\text{Sr}_x\text{MnReO}_6$ ($x = 0$, 0.5, 1, and 2) synthesized form in cubic symmetry. Rietveld analysis (Fig. 1) was performed in space group $Fm\overline{3}m$ with atomic positions Ba/(0.25, 0.25, 0.25), Mn/Re (0.5, 0.5, 0.5), Re/Mn (0, 0, 0), and O ($x$, $x$, $x$), where $x$ is the only variable-atomic-position parameter that defines Mn-O and Re-O distances. Lattice parameters, atomic position $x$, and Mn-O, Re-O distances as well as goodness of fit parameters are presented in Table I. With increasing substitution of Sr$^{2+}$ for Ba$^{2+}$ the lattice parameter decreases according to Vegard’s law (Fig. 2).

The Mn-O-Re angles are all 180° by symmetry. The Rietveld refinement is consistent with virtually 100% order of Mn and Re on $B^\prime$ and $B''$ sites of the double perovskite (Table I). The level of Mn/Re disorder (Table I) was found during the Rietveld analysis by refining Mn and Re occupancies on two different B sites in the double-perovskite structure. Constraints were set so that each B site could be occupied by a mixture of Mn$^{2+}$ and Re$^{6+}$ with a total occupancy.

TABLE I. Structural and magnetic data of $\text{Ba}_2\text{Sr}_x\text{MnReO}_6$.

<table>
<thead>
<tr>
<th>$x$</th>
<th>0</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>$\mu$ ($\mu_B$)</th>
<th>$\theta$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>8.186(1)</td>
<td>8.142(1)</td>
<td>8.096(1)</td>
<td>8.001(2)</td>
<td>400–600 K</td>
<td>5.33(4)</td>
</tr>
<tr>
<td>$x$ in O ($x$, 0, 0)</td>
<td>0.242(9)</td>
<td>0.243(8)</td>
<td>0.244(8)</td>
<td>0.243(7)</td>
<td>5.40(4)</td>
<td></td>
</tr>
<tr>
<td>Mn-O distance (Å)</td>
<td>2.109(7)</td>
<td>2.087(6)</td>
<td>2.073(6)</td>
<td>2.052(6)</td>
<td>5.40(2)</td>
<td></td>
</tr>
<tr>
<td>Re-O distance (Å)</td>
<td>1.984(7)</td>
<td>1.984(6)</td>
<td>1.975(6)</td>
<td>1.949(6)</td>
<td>5.44(2)</td>
<td></td>
</tr>
<tr>
<td>Level of Mn-Re disorder (%)</td>
<td>1.8(3)</td>
<td>2.2(3)</td>
<td>2.8(3)</td>
<td>0.7(2)</td>
<td>0.9896</td>
<td></td>
</tr>
<tr>
<td>$R_p$ (%)</td>
<td>7.71</td>
<td>7.93</td>
<td>7.18</td>
<td>7.11</td>
<td>0.9609</td>
<td></td>
</tr>
<tr>
<td>$R_{wp}$ (%)</td>
<td>10.49</td>
<td>10.24</td>
<td>9.49</td>
<td>9.58</td>
<td>0.9609</td>
<td></td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>3.791</td>
<td>4.138</td>
<td>3.382</td>
<td>5.615</td>
<td>0.9609</td>
<td></td>
</tr>
<tr>
<td>Tolerance factor $t$</td>
<td>1.0183</td>
<td>1.0040</td>
<td>0.9896</td>
<td>0.9609</td>
<td>0.9609</td>
<td></td>
</tr>
</tbody>
</table>
FIG. 2. Dependence of the lattice parameter on composition in Ba$_{2-x}$Sr$_x$MnReO$_6$.

of 1 and both B sites together can be occupied by a total one Mn$^{2+}$ and one Re$^{6+}$. The Mn-Mn and Re-Re distances are very large (5.789 Å), which suggests that direct Mn-Mn and Re-Re interactions are unlikely. The Mn-O-Re distances are 4.00–4.09 Å. The Re-O distances (1.95–1.98 Å, Table I) are larger than those in ReO$_3$ (1.84 Å, Re in octahedral coordination). On the other hand, Mn-O distances (2.05–2.11 Å) are shorter than those in MnO (2.223 Å, Mn in octahedral coordination). Based on the unit cell data reported by Kathak et al.,$^{18}$ the Re-O distance in their Ba$_2$MnReO$_6$ is 1.921 Å, which is lower, while the Mn-O distance is 2.162 Å, which is larger than in our compounds. The differences are most likely due to differences in the techniques of preparation; e.g., they used metallic Re as a starting material. Kathak et al. compare their Ba$_2$MnReO$_6$ lattice parameter [8.16(6) Å] to that of Ref. 17 (8.181 Å) which is closer to our value [8.1865(1) Å]. The Re-O distance [1.984(7) Å] in our Ba$_2$MnReO$_6$ is slightly smaller than that [1.996(2) Å] in Ba$_2$FeReO$_6$ (Ref. 20). Based on the effective ionic radius from Shannon,$^{13}$ Ba$_{1.5}$Sr$_{0.5}$MnReO$_6$ has a tolerance factor (Table I) closest to 1.

Information about the effective oxidation states of Mn and Re and the local structural distortions around these ions is provided by x-ray absorption spectroscopic investigations. Specifically the chemical shift of an atomic absorption edge to higher energy, with increasing formal oxidation state of that atom, is the simplest and most commonly used XAS valence indicator. Figure 3(a) shows the Mn-K edge of the double-perovskite compounds Ba$_2$MnReO$_6$ and Sr$_2$MnReO$_6$ along with the MnO (Mn$^{2+}$) and LaMnO$_3$ (Mn$^{3+}$) standards. The proximity of the main Mn edge of the double perovskites to that of MnO standard near the absorption coefficient $\mu = 1.0$ [see box in Fig. 3(a)] and the prominent A feature at the onset of the double-perovskite spectra are consistent with a Mn$^{2+}$ assignment. The prominent B-feature peak at the edge, in Fig. 3(a), involves 4$p$ final states. It is worth noting that the A = Sr material manifests a distinctly simpler, more intense 4$p$ feature, whereas the A = Ba spectrum exhibits a distinct 4$p$ feature splitting.

The $L_{2,3}$ edges of transition metals are dominated by very intense “white line” (WL) features due to transitions into final $d$ states. For low-$d$-count perovskite compounds, the octahedral crystal field splitting of the $d$ states, into $t_{2g}$ and $e_g$ multiplets, can be observed as a splitting of the WL feature into $A$-$B$ features related respectively to $t_{2g}/e_g$ final states. Accordingly the relative $A$- to $B$-feature intensity can be used as a probe of the $d$ occupancy, with increasing $A$-feature intensity correlating with decreasing $d$ occupancy. Note that the $A$-$B$ WL features are progressively less intense with increasing $d$-electron count of the standards in the bottom of Fig. 3(b). Moreover, the absorption edge shifts to higher energy with increasing formal oxidation state of the standards. The coincidence of both the position of the edge and the WL intensity of Re $L_3$ of the double perovskites in Fig. 3(b) suggests an approximate Re$^{6+}:d^1$ state. The bimodal A-$B$ WL features of the Re $L_{2,3}$ edges, for the double perovskite compounds, are clear in Figs. 3(b) and 3(c). The slight broadening of the A-$B$ features of the A = Sr compound (relative to the Ba compound) is presumably due to stronger hybridization effects accompanying the lattice compression.

A third XAS indicator of the Re$^{6+}:d^1$ state is the chemical shift of the centroid of the WL features at the Re $L_3$ edges. The centrum of the Re$^{7+}:d^0$, $L_3$ WL feature for NH$_4$ReO$_3$ is clearly shifted to higher energy than that of the double perovskites (“Re$^{6+}$”) [Fig. 3(b)]. The peak of the ReO$_3$ (Re$^{6+}$) WL lies between the bimodal WL peaks of the double perovskites, indicating that they have comparable centroids. This qualitatively supports the Re$^{6+}:d^1$ state assignment in the double perovskites.

For the Re standards the chemical shift is chronicled rather well by the peak of the WL feature as illustrated in Fig. 4. The strong A-$B$ splitting of the perovskite spectra complicates the evaluation of the WL chemical shift for our perovskite compounds. Accordingly, we have used the notion of the first moment ($E_m$) of the WL feature (defined below) to estimate the chemical shift:

$$E_m = \int_{E_H}^{E_L} E \mu(E) dE \left[ \int_{E_H}^{E_L} \mu(E) dE \right]^{-1}.$$

Alp et al.$^{21}$ used such a moment method to define Cu valence and charge transfer effects. Here the low-energy integration limit $E_L$ is chosen as $\sim 100$ eV below the edge to encompass the entire WL feature. $E_m$ is insensitive to the low-energy cutoff since the background pre-edge subtraction process results in $\mu \sim 0$ in this range. The high-energy cutoff needs to be chosen high enough to capture most of the WL feature weight, but not so high as to be in the range where the FS oscillations of $\mu$ (about 1.0) would make the moment estimate fluctuate with the choice. Accordingly, we have fixed this cutoff by the value where the absorption coefficient drops to the value of 1.5 on the high-energy side of the WL, i.e., where $\mu(E_H) = 1.5$. The $E_m$ values for the standard Re compounds, shown in Fig. 4 along with a linear inter point interpolation, clearly increase with increasing formal Re valence, though not as uniformly as the peak values of these
The values for the perovskite compounds have been indicated on the interpolated standard line in Fig. 4 and are close to $\sim 2$ that of Re$\text{O}_3$ and are therefore quantitatively consistent with Re$^{6+}$. In view of the strong covalency effects in these materials and the simplicity of our method, quantitative assignment of a formal valence would be inappropriate.

Thus in summation both the Mn and Re XAS measurements consistently support the basically Mn$^{2+}:d^5$ and Re$^{6+}:d^1$ $B'/B''$-site character in these double perovskites.

FIG. 3. The Mn K edges of Mn standard compounds (a), Re $L_3$ edges of Re standard compounds (b) compared to those of Ba$_2$MnReO$_6$ and Sr$_2$MnReO$_6$, and Re $L_2$ edges (c) of Ba$_2$MnReO$_6$ and Sr$_2$MnReO$_6$.

FIG. 4. The WL-peak energies (triangles) for the Re standard compounds shown in the Re $L_3$-edge spectra of Fig. 3(b) plotted vs formal Re valence. The WL moment (see text) energies (squares) are plotted for these same Re $L_3$ standard spectra. The WL moment energies for Ba$_2$MnReO$_6$ and Sr$_2$MnReO$_6$ are shown as rectangles on the interpolated standard moment line.

FIG. 5. The Re $L_3$-edge WL and C features of NH$_4$ReO$_4$, Ba$_2$MnReO$_6$, and Sr$_2$MnReO$_6$. Inset: an expanded view of the C features of three same compounds along with those of ReO$_2$ and ReO$_3$. Additional information on the Re local environment can be gleaned from the Re $L_3$-edge XAS spectra shown in Fig. 5 on an energy range encompassing the prominent fine-structure C feature. This feature can be regarded as either the first of the ligand-shell extended x-ray-absorption fine-structure (EXAFS) oscillations (with multiple scattering) or standards. $E_m$ values for the perovskite compounds have been indicated on the interpolated standard line in Fig. 4 and are close to (but just below) that of ReO$_3$ and are therefore quantitatively consistent with $\sim$Re$^{6+}$. In view of the strong covalency effects in these materials and the simplicity of our method, quantitative assignment of a formal valence would be inappropriate.

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The paramagnetic part of the reciprocal susceptibility is significantly lower than that of ReO$_3$, indicating a covalency in the ReO$_3$ compound leads to a broadening of x-ray diffraction results. The more localized Re relative Re-O bond length dilatation, consistent with the perovskites may contribute to their more resolved x-ray data were possible for a high-temperature FM Curie-Weiss law 22 or that the magnetic contribution from one sublattice is much smaller than that from the antiparallel other.

The magnetic parameters of the title compounds are presented in Table I. Néel’s generalization of the Curie-Weiss law 22, 23 [Eq. (4)] suggests that the Curie constants are additive. In this case the theoretical spin-only paramagnetic effective moment for a d$^5$-d$^4$ ferrimagnetic system should be $\sqrt{5}(5+2) + 1(1+2) = 6.16 \mu_B$ per formula unit. However, the vast majority of published data 24–28 on supposedly ferrimagnetic double perovskites show that the observed paramagnetic effective moment is close to or less than the calculated one with the assumption that the net moment reduction is present due to antiparallel spin alignment even far above the transition temperature. That is, for example, for the ferrimagnetic system with x and y unpaired electron sublattices the paramagnetic effective moment corresponds to $\sim (x - y)$ unpaired electrons.

The paramagnetic effective moments ($\mu$) of all the compounds obtained from the Curie-Weiss fit in the 120–400 K range are $\mu = (4.61–4.82) \mu_B$ and very close to the spin-only value calculated for four unpaired electrons [4.90$\mu_B = \sqrt{n}(n+2)$, where $n = 4$]. This is in line with the discussion in the previous paragraph, although our measurements taken in the 400–600 K range show that the paramagnetic moments are higher [(5.33–5.44)$\mu_B$], but they are still below the expected 6.16$\mu_B$ (Table I). Due to the possibility of short-range order well above $T_N$, care must be exercised in evaluating the temperature dependence of reciprocal susceptibility.

In Fig. 7(a) the magnetization loops as a function of field (H) are shown for the compounds at 5 K. The extrapolated saturation moment is close to the net moment of the projection of antiparallel spin d$^5$-d$^4$ electrons (4$\mu_B$), being the largest for Ba$_5$Sr$_3$MnReO$_6$, the compound with the tolerance factor closest to 1 (Table I, $x = 0.5$) and the lowest for Sr$_2$MnReO$_6$ with the $t < 1$ (Table I, $x = 2$).

For all the compounds except for Sr$_2$MnReO$_6$ there are virtually no differences between the zero-field-cooled (ZFC) and field-cooled (FC) hysteresis loops. The coercive field ($H_c$) of Ba$_5$MnReO$_6$ and that of Ba$_5$Sr$_3$MnReO$_6$ are similar and are about 4800 Oe. $H_c$ of BaSrMnReO$_6$ is larger, 6500 Oe. Finally, the $H_c$ of Sr$_2$MnReO$_6$ derived from ZFC is the largest, 26,400 Oe.
The high coercivity in Sr$_2$MnReO$_6$ may be due to relatively large concentration of defects that strongly hinder magnetic domain wall motion or single-domain particles with very high magnetic anisotropy. The former case is unlikely, because the electronic defects discussed below, even when originating from oxygen deficiencies, would not affect magnetic domain wall motion. In addition, the material is unlikely to have any induced structural defects because no special synthetic techniques were employed. Thus a very high intrinsic magnetic anisotropy, such as magnetocrystalline anisotropy, and not the one resulting from particle shape, is the most likely reason for the observed high coercivity. That and the presence of single-domain particles with low interparticle exchange coupling could produce conditions where the direction of magnetization can be changed only by very large fields. Large magnetocrystalline anisotropy with an easy axis occurring in uniaxial crystal systems, in contrast to one with an easy plane occurring in cubic systems, usually leads to high coercivity because the sample cannot demagnetize without the magnetization rotating to a hard direction. Undetectable by PXD, deviation from cubic symmetry of Ba$_{2-x}$Sr$_x$MnReO$_6$ with increasing Sr content (tolerance factor deviating from 1) may lead to the observed dramatic increase in the coercive field, consistent with the above discussion. However, detailed micromagnetic studies would be required to explain unambiguously the observed phenomena.

Many authors have reported small if any moments for Re$^{6+}$:$5d^{1}$ and Re$^{5+}$:$5d^{2}$ ions in an octahedral crystal field. Khattak et al.$^{18}$ obtained 0, 0.2µ$_{B}$, or 1µ$_{B}$ (depending on the data fitting) on Re$^{6+}$ from neutron diffraction of Ba$_2$MnReO$_6$; Fang et al.$^{3}$ regarded rhenium in Sr$_2$FeReO$_6$ as nonmagnetic; Wiebe et al.$^{29}$ proposed no magnetic contribution from Re$^{5+}$ in La$_3$Re$_3$MnO$_{19}$; Bramnik et al.$^{30}$ reported temperature-independent paramagnetism in Sr$7$Re$_4$O$_{19}$ and in another paper Bramnik et al.$^{31}$ reported a moment of 0.80µ$_{B}$ per Re$^{6+}$ in Sr$_{11}$Re$_4$O$_{24}$. From general considerations the effective moment of a heavy element such as Re$^{6+}$ could be reduced by spin-orbit coupling and the covalency broadening of the Re $5d$ orbitals.

In our compounds the saturation moment is lower than the expected, 4µ$_{B}$, less than 3.3µ$_{B}$ for Ba$_2$MnReO$_6$ and about 3.5µ$_{B}$ for Ba$_3$MnReO$_8$. Moreover, if we assume that there is very little moment on Re$^{6+}$ [as was determined by neutron diffraction on Ba$_2$MnReO$_6$ (Ref. 18)], the expected net effective moment should be even higher than 4µ$_{B}$ because of the reduced cancellation of Mn$^{2+}$:$d^{5}$-Re$^{6+}$:$d^{1}$ antiferromagnetic (AF) contributions. The absence of moment on Re$^{6+}$...
would lead to purely FM interactions among Mn\(^{2+}\) ions, which is supported by the positive Weiss constants (Table I) typical for ferromagnets; however, because of the slight parabolic curvature of 1/\(x\) vs \(T\) plots [Fig. 6(b)] characteristic of ferrimagnets, we believe that there is some moment present on Re\(^{6+}\). One possible explanation of the lower than expected saturation moment of our compounds could be due to the reduction of moment on Mn\(^{2+}\) by covalency effects. This cannot be ruled out since a covalent superposition of \(d\) configurations is common in such compounds. Also, since the saturation moment is a projection of ordered moments, sublattice mismatch by Mn\(^{2+}\) and Re\(^{6+}\) ions would produce regions of AF-coupled Mn\(^{2+}\)-Mn\(^{2+}\) ions and reduce the net moment. Ideally 1% of sublattice mismatch disorder would induce 2% of net moment decrease. As determined by Rietveld refinement the studied compounds have some sublattice disorder (0.7%–2.8%) (Table I) that could be the cause of the reduced saturation magnetic moment and electronic disorder found by resistivity measurements discussed later.

The magnetic properties of Sr\(_2\)MnReO\(_6\) deserve special attention. Unlike the other three, Sr\(_2\)MnReO\(_6\) exhibits a nonequilibrium magnetization state in ZFC even in a high field of 5 T [different \(M-H\) loops in Fig. 7(a) and \(M-T\) curves in Fig. 8(a)]. The ZFC magnetization has an almost logarithmic dependence on time [Fig. 8(b)], which is most likely caused by slow magnetic-domain reorientation in the field. The values of the ZFC magnetizations at 5 K in Figs. 8(a) and 8(b) do not match as expected for nonequilibrium states and also may be influenced by slightly different rates of cooling.
Closer examination of the ZFC $M-H$ loops of $\mathrm{Sr}_2\mathrm{MnReO}_6$ reveals a peculiar behavior depending on temperature [Fig. 7(b)]. Although the coercive field decreases with increasing temperature as expected, unusual features are observed at 5 K, such as discontinuities at about 2.5 T and $-2.5$ T which are reproducible. Furthermore, the beginning of the loop (from 0 T and up) is quite flat, whereas at 30 and 70 K there are no discontinuities in magnetization and the beginnings of the loops are steep. The discontinuities could be attributed to flips of frustrated spins on $\text{Re}^{6+}$ ions; however, we cannot reach an unambiguous conclusion on this without neutron diffraction studies in various magnetic fields, which will be the subject of a separate study.

Resistivity measurements presented in Fig. 9 indicate that the compounds are highly resistive; reliable measurements below 70 K could not be obtained. The linear dependence of the logarithm of the resistivity versus $T$ is consistent with a 3D variable-range hopping type of conduction. Sleight and Weihert\textsuperscript{17} suggested that the Mn-O and Re-O molecular levels are too different in energy to allow for mixing and there are no Mn-O-Mn or Re-O-Re pathways. This would predict a band gap in the electronic structure. However, local distortions, low-level Mn-Re disorder, or slight oxygen nonstoichiometry could induce an impurity band near the Fermi level. Anderson localization of electrons in the impurity band could lead to variable-range hopping. The barium member of the series has lower resistivity than the strontium one despite the fact that the $\text{Mn}/\text{Re}-\text{O}$ distances are shorter in the latter.

Magnetoresistance (MR) measurements (Fig. 10) indicate low negative MR for all compounds above 120 K. It is unlikely that one would find large MR in compounds with such high resistivities. There is a small anomaly in the MR around 120 K (corresponding to $T_N$) for all compounds, except $\text{Ba}_2\text{MnReO}_6$. In contrast, the MR of $\text{Ba}_2\text{MnReO}_6$ becomes positive 14% below 120 K. This behavior is reproducible; field-dependent MR measurements at 80 K also show that the MR of $\text{Ba}_2\text{MnReO}_6$ is indeed positive [Fig. 11(a)].

The field-dependent MR’s of $\text{Ba}_{1.5-}\text{Sr}_{0.5}\text{MnReO}_6$ and $\text{BaSrMnReO}_6$ confirm their negative signs [Figs. 11(b) and 11(c)].

Both negative and positive magnetoresistance are possible in the variable-range hopping regime.\textsuperscript{32} A variety of behavior can be observed by changing the temperature, magnetic field, doping level, and so on.\textsuperscript{32–35} Negative MR can be due to a reduction of scattering and field suppression of localization; positive MR can be due to Zeeman spin splitting and spin-orbit scattering.\textsuperscript{32} The total MR is a combination of the additive contributions. All of our samples have a negative MR above $T_N$, and only $\text{Ba}_2\text{MnReO}_6$ has a positive MR below $T_N$. However, the MR curves of the other samples show some trend to go in the positive region at lower temperatures. The very high resistivities of the samples precluded taking measurements at temperatures below 80 K.

In our system the negative MR above $T_N$ can be the result of the reduced scattering of magnetically disordered paramagnetic states in an applied field with this contribution dominating over all other effects. Below $T_N$, where the spins are ordered and scattering is already low even without a field, other effects, such as spin-orbit scattering, dominate the total MR, making it positive.\textsuperscript{34}

IV. CONCLUSIONS

$\text{Ba}_{2-x}\text{Sr}_x\text{MnReO}_6$ ($x = 0, 0.5, 1, 2$) double perovskites were synthesized and their magnetic and transport properties were investigated. Based on powder diffraction data all the compounds possess cubic symmetry. $\text{Mn}^{2+}$ and $\text{Re}^{6+}$, whose formal oxidation states were determined by x-ray absorption spectroscopy, virtually completely order on the $B$ site of the double-perovskite structure. We observe ferrimagnetic order with $T_N$ around 120 K for all compounds; however, the Weiss constants are positive. The saturation magnetic moments are between 3.3$\mu_B$ and 3.8$\mu_B$, which are lower than the expected 4$\mu_B$, with the largest value observed for $\text{Ba}_{1.5}\text{Sr}_{0.5}\text{MnReO}_6$ and the lowest for $\text{Sr}_2\text{MnReO}_6$. We attribute the lowering of the saturation moment to a low degree of disorder on the $B$ sites and possible distortions from cubic symmetry. $\text{Sr}_2\text{MnReO}_6$ exhibits a nonequilibrium magnetization state when zero-field cooled in 5 T. In addition, discontinuities observed in the $M-H$ loops of $\text{Sr}_2\text{MnReO}_6$ were attributed to flips of frustrated spins on $\text{Re}^{6+}$ ions. All compounds have variable-range-hopping-type conduction with low negative magnetoresistance above 120 K. The very high resistance of the compounds precluded resistivity measurements below 80 K. $\text{Ba}_2\text{MnReO}_6$ exhibits an unusually high (14% in 5 T) positive MR at 80 K while the MR’s of the other compounds remain negative in the temperature range measured.

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LARGE EFFECTS OF A-SITE AVERAGE CATION SIZE . . .

024406-9


Moments deduced from raw data published in Ref. 2.


Moments deduced from raw data published in Ref. 18.


