Trimers of MnO$_6$ octahedra and ferrimagnetism of Ba$_4$NbMn$_3$O$_{12}$

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Keywords: magnetism, triangular lattice, manganese trimer, ferrimagnetism

Abstract

Ba$_4$NbMn$_3$O$_{12}$ is reported, synthesized by a solid state method in air. The crystal structure, determined by performing refinements on room temperature powder x-ray diffraction data by the Rietveld method, consists of Mn$_3$O$_{12}$ trimers in the configuration of three face-sharing MnO$_6$ octahedra, with the trimers arranged in triangular planes. An effective moment of 4.82 $\mu_B$/f.u is observed and competing antiferromagnetic and ferromagnetic interactions between Mn ions are inferred from the Weiss temperature of $-4$ K and the ferrimagnetic ordering transition of approximately 42 K. Ba$_4$NbMn$_3$O$_{12}$ is a semiconductor with a transport activation energy of 0.37 eV.

Introduction

Manganese-based perovskites have been intensively researched due to the metal-insulator (MI) transitions and colossal magnetoresistance (CMR) [1–4] in this family. The interesting properties have been attributed in part to the competition between a ferromagnetic metallic state and an antiferromagnetic insulating state, and the presence of charge-ordering. Manganates are also well known due to other structural, electronic, and magnetic characteristics [5, 6]. In the hexagonal perovskite RMnO$_3$ phases, for example, the electric polarization is reported to be the result of a structural transition [7] and the improper nature of ferroelectricity to a network of coupled structural and magnetic vortices that induce domain wall magnetoelectricity and magnetization [8].

Of particular interest for CMR are materials with lower structural dimension based on the Ruddlesden-Popper series [9], but quasi-1D materials are also of interest [10]. Instead of sharing corners in a 3D network as in corner-sharing perovskites, the MnO$_6$ octahedra in the quasi-1D materials can share faces with each other to form Mn$_2$O$_9$ dimers or Mn$_3$O$_{12}$ trimers. These Mn mini-clusters are isolated from other clusters in the structure. This type of MnO$_6$ configuration is relatively uncommon because the Mn-Mn distances of about 2.5 Å within the clusters are shorter than the 3.5 Å typically found in corner-sharing geometries [11]. Oxygen deficient BaMnO$_{3-x}$ and (Ba,Sr)MnO$_{3-x}$ phases are good examples of materials where clusters of face-sharing MnO$_6$ octahedra are found [12].

In the current work, we report the synthesis and initial characterization of the mixed valent Mn$^{3+}$/Mn$^{4+}$ compound Ba$_4$NbMn$_3$O$_{12}$. The crystal structure of this previously unreported phase, which is much like that of Ba$_4$REMn$_3$O$_{12}$ ($RE$ = Ce, Pr) [13], consists of face-sharing MnO$_6$ octahedra forming Mn$_3$O$_{12}$ trimers with their long axes aligned along the hexagonal c axis of the trigonal symmetry crystallographic cell. From magnetic susceptibility measurements, the effective magnetic moment is found to be 4.82 $\mu_B$/f.u., consistent with a simple spin configuration within the trimers. Resistivity measurements show that Ba$_4$NbMn$_3$O$_{12}$ is semiconducting with a transport gap of 0.37 eV. The current phase is chemically and structurally distinct from recently reported Ba$_8$MnNb$_6$O$_{24}$, which, among other differences, does not appear to contain any face shared octahedral [14].
Methods

Polycrystalline samples of Ba$_4$NbMn$_3$O$_{12}$ were synthesized by solid-state reaction using BaCO$_3$, MnO$_2$, and Nb$_2$O$_5$ (Alfa Aesar, 99.9%, 99.999%, and 99.5%, respectively) as starting materials. Reagents were mixed thoroughly in the appropriate ratio, placed in an alumina crucible, and heated in air at 900 °C for 24 h. The resulting powder was re-ground, pressed into a pellet and heated in air at 1100 °C for 24 h, and then at 1300 °C for 12 h. The phase purity and crystal structure were determined through powder x-ray diffraction (PXRD) using a Bruker D8 Advance Eco with Cu Kα radiation and a LynxEye-XE detector. The structural refinements were performed with GSAS [15]. The crystal structure drawing was created by using the program VESTA [16].

The magnetic susceptibility of Ba$_4$NbMn$_3$O$_{12}$ powder was measured by a Quantum Design Physical Property Measurement System (PPMS) DynaCool equipped with a VSM option. The magnetic susceptibility of Ba$_4$NbMn$_3$O$_{12}$, defined as $M/H$, where $M$ is the sample magnetization and $H$ is the applied field, was measured at the field of $H = 1$ kOe (at 1 kOe applied field, the $M$ versus $H$ curve is linear for all temperatures above the magnetic ordering temperature) from 1.8 K to 300 K; some additional measurements were performed in an applied field of 100 Oe. (The 1 kOe data allow us to characterize the magnetic susceptibility above the ordering temperature. The 100 Oe data allow us to characterize the difference between field-cooled and zero field-cooled susceptibilities below the temperature of the magnetic transition.) The resistivity of Ba$_4$NbMn$_3$O$_{12}$ was measured by the DC four-contact method in the temperature range 200 K to 350 K with the PPMS. The sample was pressed, sintered, and cut into pieces with the approximate size 1.0 × 2.0 × 1.0 mm$^3$. Four Pt contact wires were connected to the sample using silver paint. The specific heat was measured from 1.8 K to 200 K by a PPMS DynaCool equipped with a heat capacity option.

Results and discussion

The powder x-ray diffraction pattern and structural refinement of Ba$_4$NbMn$_3$O$_{12}$ are shown in figure 1. The structure of Ba$_4$NbRu$_3$O$_{12}$ [17] was used as the starting model. Ba$_4$NbMn$_3$O$_{12}$ crystallizes in a rhombohedral structure with the space group R-3m (No. 166). Refinements in which the Mn to Nb ratio was allowed to vary from 3:1 or Nb/Mn site mixing was permitted were not satisfactory. The lattice parameters and structural parameters for Ba$_4$NbMn$_3$O$_{12}$ are summarized in table 1. The structure consists of three MnO$_6$ octahedra connected by face-sharing to form Mn$_3$O$_{12}$ trimers, as shown in figure 2. The crystal structure of Ba$_4$NbMn$_3$O$_{12}$
is similar to those of two known rare-earth containing compounds Ba$_4$RE Mn$_3$O$_{12}$ (RE = Ce, Pr) [13] in the same family. The corner-sharing NbO$_6$ and Mn$_3$O$_{12}$ trimers in Ba$_4$NbMn$_3$O$_{12}$ alternate along c to generate the 12-layer hexagonal perovskite structure. Individual Mn$_3$O$_{12}$ trimers are corner-sharing with the non-magnetic NbO$_6$ octahedra, and not to other trimers, such that the magnetic coupling between trimers is of the Mn-O-Mn super-super exchange type. Within each trimer, the distance between Mn atoms is 2.4694 Å, quite short due to the face-sharing [11], favoring strong magnetic interactions between them. The Mn-O distances are 1.903 Å and 1.882 Å for the outer NbO$_6$ octahedra, reflecting a small distortion, and 1.895(4) Å for the inner MnO$_6$ octahedron, which has an ideal shape. These Mn-Mn and Mn-O bond lengths are in agreement with those of two known rare-earth containing compounds Ba$_4$REMn$_3$O$_{12}$ (RE = Ce, Pr) [13] in the same family.

The magnetic hysteresis loops for Ba$_4$NbMn$_3$O$_{12}$ from 100 K to 275 K are well fitted to the standard model of a ferrimagnet. At 150 K, the magnetization is linearly proportional to the field and there is no hysteresis loop. Because Ba$^{2+}$ and Nb$^{5+}$ (which has no electrons in d orbitals) are non-magnetic, the magnetic properties of Ba$_4$NbMn$_3$O$_{12}$ are determined by the intertrimer and intratramer interactions of the Mn$_3$O$_{12}$ units. Formally, one Mn$^{3+}$ and two Mn$^{4+}$ are found in each Mn$_3$O$_{12}$ trimer. Thus, in the paramagnetic state, where the moments fluctuate, the total magnetization per formula unit is expected to be the sum of the magnetizations of two Mn$^{4+}$ and one Mn$^{3+}$, which, should all the moments be free to respond to an applied field for temperatures below 300 K, yield a total effective moment of 6.16 (low spin Mn$^{3+}$) or 7.35 (high spin Mn$^{3+}$) $\mu_B$/f.u. This magnetic state is not compatible with the observed data. Figure 4 shows, in contrast, a schematic of two simple hypothetical magnetic states within each trimer, which, to be consistent with our magnetic data, in these simple scenarios, either two Mn$^{3+}$ bearing spin-3/2 point in the same direction and opposite to the low spin (S = 1) Mn$^{2+}$ between them or two Mn$^{4+}$ bearing spin-3/2 point in opposite directions and the Mn$^{3+}$ (high spin) with the spin-2 is between them. With this proposed magnetic coupling within the trimer, each trimer has spin-2 and a calculated effective moment of 4.90 $\mu_B$/f.u. This is in excellent agreement with the observed effective moment of 4.82 $\mu_B$/f.u in the susceptibility measurements, indicating that either of these trimer-based spin models is likely to successfully describe the magnetic state of Ba$_4$NbMn$_3$O$_{12}$ above the three-dimensional magnetic ordering temperature near 42 K. Compared to Bi$_3$Mn$_{11}$O$_{33}$ [19], for example, which has mixed-valent Mn, an effective magnetic moment of 6.27 $\mu_B$/f.u and a Curie-Weiss temperature of 222 K, both the effective moment and Curie-Weiss temperature of Ba$_4$NbMn$_3$O$_{12}$ are smaller. The strong coupling of the Mn spins within the trimers to create a magnetic Mn ‘molecule’ made of three Mn’s in the current material is consistent with what has previously been found for (Ba,Sr)MnO$_3$ phases [12, 20]. The fitted $\chi_0$ in this scenario is then a representation of the remnant susceptibility of the magnetic system after the local-only magnetic ordering has set in within the individual trimers at temperatures above 300 K.

Figure 5 shows the field-cooled (FC) and zero-field-cooled (ZFC) DC susceptibility in an applied field of 100 Oe for Ba$_4$NbMn$_3$O$_{12}$. The increases of the FC and ZFC susceptibility below 42 K reconfirm the magnetic transition temperature observed in the magnetic susceptibility data shown in figure 3, and the $\gamma$T versus T data shown in the inset defines the temperature of the magnetic transition at the same temperature through the dramatic change in the Curie constant.

The resistivity of Ba$_4$NbMn$_3$O$_{12}$ is plotted as a function of reciprocal temperature in figure 6. Resistivity data from 300 to 350 K were fit to the standard model $\rho = \rho_0 e^{E_a/RT}$, and the transport activation energy $E_a$ was calculated to be 0.37 eV. The inset shows the increase in resistivity when cooling. With the activation energy of

| Atom | Wyckoff | Occ. | x  | y  | z  | $U_{iso}$ |
|------|---------|------|----|----|----|----------|
| Ba1  | 6c      | 1    | 0  | 0  | 0.128 47(4) | 0.0344(3) |
| Ba2  | 6c      | 1    | 0  | 0  | 0.285 92(4) | 0.0304(3) |
| Nb   | 3a      | 1    | 0  | 0  | 0   | 0.0083(3) |
| Mn1  | 3b      | 1    | 0  | 0  | $\frac{1}{2}$  | 0.0195(3) |
| Mn2  | 6c      | 1    | 0  | 0  | 0.412 18(4) | 0.0146(3) |
| O1   | 18h     | 1    | 0.4776(6) | 0.5224(6) | 0.122 39(4) | 0.0212(3) |
| O2   | 18h     | 1    | 0.4908(6) | 0.5092(6) | 0.293 27(4) | 0.0127(3) |

$a = 5.718 25(3)$ Å, $c = 28.1158(3)$ Å,

$R_w = 10.30\%$, $R_p = 8.02\%$, $R_F^2 = 10.80\%$
0.37 eV, $\text{Ba}_4\text{NbMn}_3\text{O}_{12}$ is a semiconductor, similar to other trimer-based compounds ($\text{Ba}_4\text{NbRu}_3\text{O}_{12}$ and $\text{Ba}_4\text{LnRu}_3\text{O}_{12}$ and $\text{Ba}_4\text{LnIr}_3\text{O}_{12}$) \cite{17, 21}.

Figure 7(A) shows the specific heat divided by temperature of $\text{Ba}_4\text{NbMn}_3\text{O}_{12}$ measured from 1.8 K to 200 K in its main panel, with the raw $C_p$ data shown in the inset. At 200 K, $C_p$ has not yet reached the saturation value of $3NR$ ($N$ is the number of atoms), but this is often encountered in materials where different atomic masses and strong bonds between atoms lead to very high vibrational frequencies \cite{22}. Three characteristic features are seen. The $\lambda$-anomaly corresponds to the magnetic transition around 42 K and is shown in figure 7(B). In this case we employed a polynomial function fit to the data above and below the anomaly to estimate the phonon background; at this level of analysis we do not attach any significance to the function employed to estimate the phonon part. In this way the magnetic entropy change in the higher temperature range is estimated to be 0.45 J mol$^{-1}$ K$^{-1}$. This relatively weak anomaly implies that there is a significant remnant of magnetic entropy in

![Crystal structure of $\text{Ba}_4\text{NbMn}_3\text{O}_{12}$](image)

*Figure 2.* The crystal structure of $\text{Ba}_4\text{NbMn}_3\text{O}_{12}$. The NbO$_6$ octahedra (dark green) share corners with the Mn$_3$O$_{12}$ (purple) trimers made from face-shared MnO$_6$ octahedra, to form what is frequently referred to as a ‘12-layer’ hexagonal perovskite structure. Barium is green, and oxygen is red.
Figure 3. The temperature dependence of the magnetic susceptibility and the inverse of the difference between the magnetic susceptibility and the temperature independent magnetic susceptibility ($\chi_o = 3.07 \times 10^{-3}$ emu Oe$^{-1}$ mol-f.u.$^{-1}$) for Ba$_4$NbMn$_3$O$_{12}$. The applied field was 1 kOe. The red solid line is the susceptibility fit to the Curie-Weiss law for T from 100 K–275 K. The inset shows the magnetic hysteresis loops for Ba$_4$NbMn$_3$O$_{12}$ from $-2$ to $2$ T at 2 K, 25 K and 150 K. At 150 K, the magnetization is linearly proportional to the field and there is no hysteresis loop.

Figure 4. Two schematics of possible simple hypothetical arrangements for Mn$^{3+}$ (either $S = 1$ for low spin (left model) or $S = 2$ for high spin (right model)) and Mn$^{4+}$ (always $S = 3/2$ in Ba$_4$NbMn$_3$O$_{12}$. Both hypothetical arrangements yield spin-2 for each Mn$_3$O$_{12}$ trimer, $\mu_{\text{eff}} = 4.90 \mu_B$/f.u., which compares very favorably to the observed $\mu_{\text{eff}} = 4.82 \mu_B$/f.u.
Figure 5. Field Cooled (FC) and Zero Field Cooled (ZFC) DC magnetic susceptibility in an applied field of 100 Oe for Ba$_4$NbMn$_3$O$_{12}$ from 2–300 K. The inset shows the first derivative of magnetic susceptibility multiplied by temperature as function of temperature (a measure of the Curie constant). The magnetic transition temperature is found to be 42.4 K by extrapolating the derivative curves.

Figure 6. The resistivity of a sintered polycrystalline pellet of Ba$_4$NbMn$_3$O$_{12}$ as a function of temperature (Inset) and inverse temperature (Main Panel). The data was fit to the model $\rho = \rho_0 e^{E_a/kT}$ (red line) with $E_a = 0.37$ eV.
Ba$_4$NbMn$_3$O$_{12}$ below the 42 K transition. The specific heat in the lower temperature range is shown in more detail in Figure 7(C), which shows another entropy loss at 5–6 K. In this case the phonon part of the specific heat is estimated by a Debye-Einstein model, again to which we attribute no physical significance at this level of analysis. The magnetic entropy at this lower temperature, which does not clearly yield a feature in the magnetic susceptibility, is found to be 2.67 J mol$^{-1}$ K$^{-1}$. For these two temperature regions only, only one-fourth of the magnetic entropy expected for an $S = 2$ Heisenberg system is recovered as shown in Figure 7(D). There is a more subtle feature in $C_p/T$ at around 30 K that may hold a significant amount of entropy, but we cannot reasonably analyze it at this time. Aside from the most general conclusions described here, analysis of the specific heat cannot be considered as well-established at present, as we have not been able to make a non-magnetic analog to use to best model the phonon contribution to the specific heat of this material.

**Conclusion**

Ba$_4$NbMn$_3$O$_{12}$, a previously unreported material synthesized by a solid state method, crystallizes in a 12-layer hexagonal perovskite unit cell with the $R$-3$m$ space group. Differences in the Mn–O bond lengths in the octahedra, although subtle, may reflect the presence of charge ordering, although we do not believe that the distinction is great enough to warrant assigning specific charge states to specific octahedra at the present time. The material has a high, temperature-dependent resistivity, indicating that it is semiconducting, with a transport activation energy of 0.37 eV measured on a sintered polycrystalline pellet. From magnetic susceptibility measurements, the Curie-Weiss temperature is calculated to be $-4$ K, indicating the presence of competing ferromagnetic and antiferromagnetic interactions between Mn trimers. The effective moment of 4.82 $\mu_B$/f.u agrees with the value of 4.90 $\mu_B$/f.u that can be deduced from a simple hypothetical magnetic model in which the spins within the trimer are essentially already ordered by 300 K, although the trimer-trimer ordering does not
occur until much lower temperatures. The ordering of the trimer spins with respect to those in other trimers is what most likely gives rise to the magnetic transition observed around 42 K. Heat capacity measurements show a weak anomaly at around 42 K, supporting the magnetic ordering transition seen in magnetic susceptibility. Only small amounts of magnetic entropy are observed through the specific heat, consistent, in principle, with the proposal that most of the magnetic entropy is lost at higher temperature than is studied here. A non-magnetic analog for this system would be of interest to account for the phonon contribution in the specific heat so that a more detailed interpretation of the entropy will be possible. Magnetic neutron diffraction will also be of future interest to establish the nature of the magnetism in this material. As for Mn-based conventional perovskites, hexagonal Mn-based perovskites appear to display rich magnetic phenomena.

Acknowledgments

This work was supported in its entirety by the Department of Energy Division of Basic Energy Sciences, through the Institute for Quantum Matter, grant DE-FG02-08ER46544. The authors thank Daniel Khomskii for valuable discussions about manganite magnetism.

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