# Structure and Magnetic Order in the Series $Bi_xRE_{1-x}Mn_{0.5}Fe_{0.5}O_3$ (RE = La, Nd)

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Due to the recent interest in multiferroic materials, many studies have focused on the influence of lone-pair effects on structure, as it has the potential to induce noncentro-symmetric symmetry (A-site driven ferroelectrics) [1]. Surprisingly few ambient pressure pure Bi A-site perovskites are known, including $BiTi_{3/8}Fe_{1/4}M_{3/8}O_3$ (M = Mg, Ni) [2], $BiFeO_3$ [3], $BiFe_{1-x}Mn_xO_3$ (x = 0.1, 0.2) [4], and $Bi_2Mn_{4/3}Ni_{2/3}O_6$ [5]. Here we examine the influence of $Bi^{3+}$ on the structure and properties of the rare-earth containing perovskites $REMn_{0.5}Fe_{0.5}O_3$ (RE = La, Nd), and determine the limit of substitution. $Bi_{0.5}La_{0.5}Mn_{0.5}Fe_{0.5}O_3$ has been reported as a cubic material [6]; other compositions have not been previously studied. The end members $REMn_{0.5}Fe_{0.5}O_3$ are antiferromagnetic insulators with the Pnma structure, while the rhombohedral bismuth end member $BiMn_{0.5}Fe_{0.5}O_3$ has been reported as a high pressure phase exhibiting antiferromagnetic order.

Powders were prepared by firing pelletized, intimate mixtures of binary metal oxides; a range of firing temperatures with intermediate regrinding steps were required, with final firing temperatures increasing with increasing lanthanide content. Laboratory X-ray diffraction data were collected to examine phase purity for each compound as well as to obtain Rietveld refinement quality data (Siemens D5005 and Panalytical X'Pert Pro; Cu $K_\alpha$).

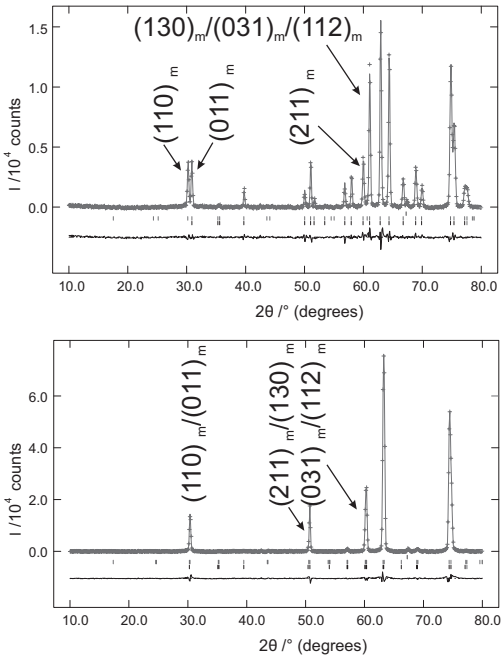


**Fig 1.** *Rietveld refinement of powder neutron diffraction data collected at 4K for (a) $Bi_{0.5}Nd_{0.5}Mn_{0.5}Fe_{0.5}O_3$ and (b) $Bi_{0.5}La_{0.5}Mn_{0.5}Fe_{0.5}O_3$. The peaks with magnetic contributions are indexed to the* **k** *= (000) magnetic cell.*

Variable temperature powder neutron diffraction data were collected on the C2 diffractometer at the Canadian Neutron Beam Center, Chalk River Laboratories. A combination of high bank data (43°-113° 2θ; 1.3308 Å) and low bank data (3.4° – 83° 2θ; 2.3720 Å) were collected at 300 K and 4 K. A combined refinement of powder X-ray diffraction data and powder neutron diffraction data was carried out for comparison with both the GSAS [7] and Fullprof [8] programs. The resulting model was applied at 4 K to refine a combination of crystal and magnetic structure (Figure 1). Variable temperature data were refined using the batch mode of Fullprof. Additional long wavelength (2.2720 Å) data were typically collected at 10 K; in 25 K intervals from 25 K to 150 K; in 10 K intervals from 150 K to 220 K; in 5 K intervals from 220 K to 260 K; at 270 K, 280 K, 290 K, and 300K. These data were used to follow the variation in magnetic moment with temperature, and to determine the magnetic ordering temperature.

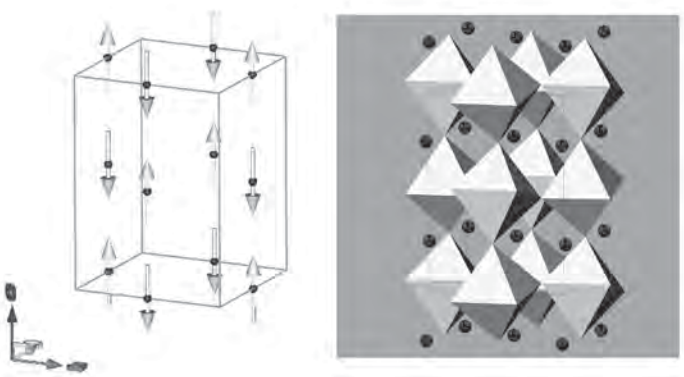

**Fig 2.** *G-type antiferromagnetic structure (left) and crystal structure (right) common to both $Bi_xLa_{1-x}Mn_{0.5}Fe_{0.5}O_3$ and $Bi_xNd_{1-x}Mn_{0.5}Fe_{0.5}O_3$ shown in the Pnma setting. The structure of $Bi_{0.3}La_{0.7}Mn_{0.5}Fe_{0.5}O_3$ is centrosymmetric C2/c, with a structure closely related to that of the other phases, including a slight monoclinic distortion (90.19(±1)°) in the unit cell.*

A combination of neutron diffraction and high resolution X-ray diffraction data indicate that these Bi doped perovskites remain orthorhombically distorted Pnma perovskites up to x = 0.5; an exception is found for x = 0.7 when RE = La, which refines in C2/c (Figure 2). The volume is shown to decrease with increasing rare-earth content for La and Nd containing compounds (Figures 3 and 4). Each of the axes increase with increasing temperature with the exception of the b axis for the Nd phases, which display a slow variation with temperature, and in fact display negative thermal expansion along this axis in the higher temperature range.

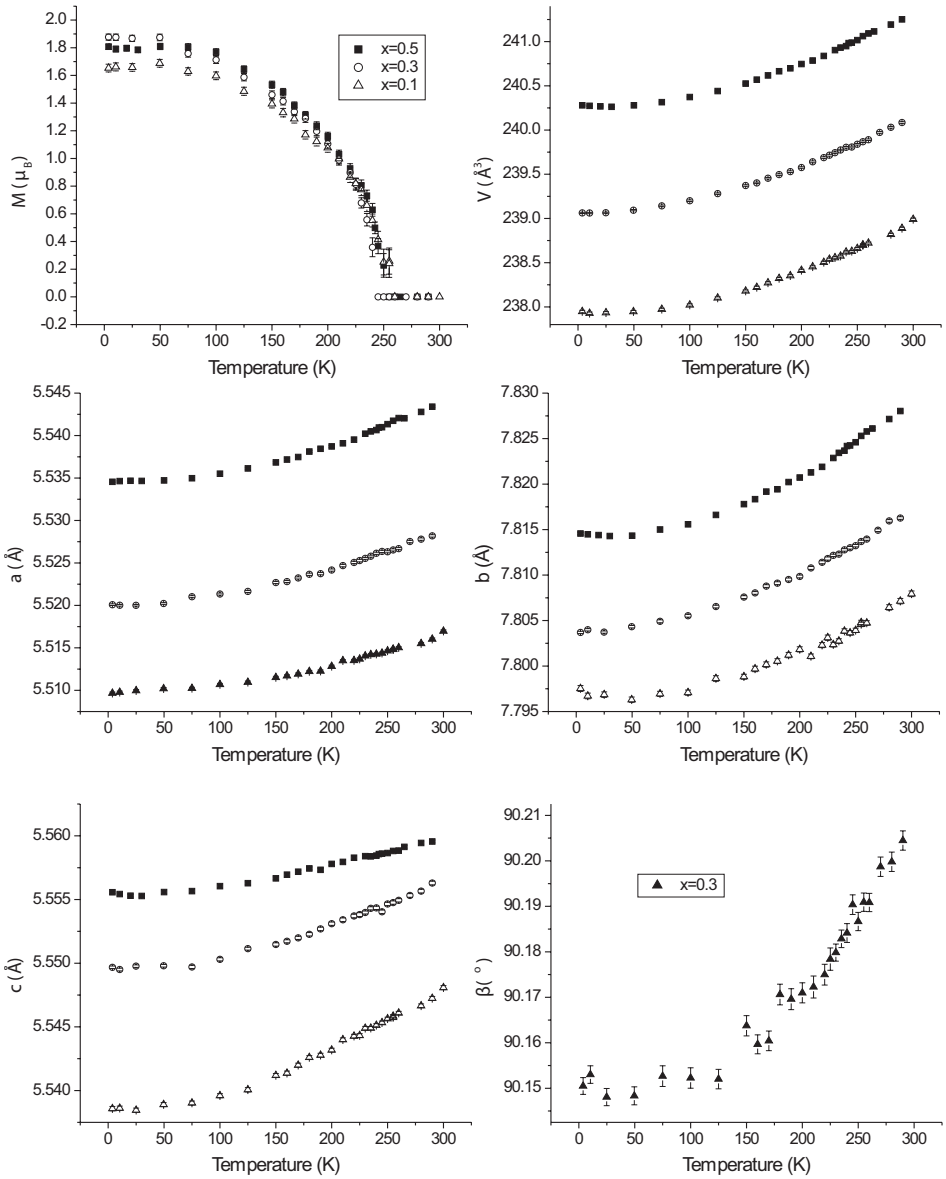


***Fig 3.*** *Variation in magnetic moment and lattice parameters versus temperature for $Bi_xLa_{1-x}Mn_{0.5}Fe_{0.5}O_3$ from neutron powder diffraction data.*

***Table 1.*** *Refinement results for $Bi_xRE_{1-x}Fe_{0.5}Mn_{0.5}O_3$ (x = 0.1, 0.3, 0.5)*

| RE | x | Space Group | a* (Å) | b (Å) | c (Å) | $\chi^2$ | M† (μB) | $T_N$ (K) | V (Å3) |
|---|---|---|---|---|---|---|---|---|---|
| La | 0.1 | Pnma | 5.5185(1) | 7.8142(1) | 5.55000(8) | 2.252 | 1.66(4) | 243(2) | 239.331(7) |
| La | 0.3 | C2/c | 5.52951(7) | 7.8203(1) | 5.56113(7) | 2.258 | 1.88(2) | 241(1) | 240.475(6) |
| La | 0.5 | Pnma | 5.54268(5) | 7.82918(6) | 5.56371(4) | 2.169 | 1.81(2) | 243(2) | 241.479(4) |
| Nd | 0.1 | Pnma | 5.6337(1) | 7.7078(2) | 5.4357(1) | 1.943 | 2.32(3) | >300 | 236.038(8) |
| Nd | 0.3 | Pnma | 5.63521(3) | 7.73337(4) | 5.43788(2) | 3.116 | 2.14(3) | 253(2) | 236.978(2) |
| Nd | 0.5 | Pnma | 5.60615(6) | 7.76954(8) | 5.44513(5) | 2.378 | 2.15(2) | 252(1) | 237.175(5) |

**lattice parameters at 300 K; $\chi^2$ is for the combined refinement of neutron/X-ray powder diffraction data at 300 K; M is the refined moment at 4 K; $T_N$ is the magnetic ordering temperature; the space group setting for RE = La and x = 0.3 given above is I112/b, for ease of comparison with Pnma phases, with an γ angle of 90.19(±1)°*

Analysis of magnetic reflections, the magnetic structure is of the antiferromagnetic G-type. The ordering temperature reported in Table 1 was determined by a best fit to the expression for a critical exponent.

Magnetic ordering is shown to occur in the range of 245 K to 260 K, with the exception of $Bi_{0.1}Nd_{0.9}Mn_{0.5}Fe_{0.5}O_3$. The phase $Bi_{0.1}Nd_{0.9}Mn_{0.5}Fe_{0.5}O_3$ displays a unique temperature dependence with respect to both lattice parameters and magnetic moment. This behavior has been attributed to phase segregation, observed in the microprobe analysis for this phase. The $Bi_{0.1}Nd_{0.9}Mn_{0.5}Fe_{0.5}O_3$ phase is particularly challenging to prepare, requiring relatively high firing temperatures (≥ 1000°C) to observe a pattern essentially free of impurity lines, at which point phase segregation was observed. Microprobe analysis indicates that the other members of the series are essentially homogeneous on the micron scale, with minor impurities present in the form of Bi/RE rich oxide phases.


### References

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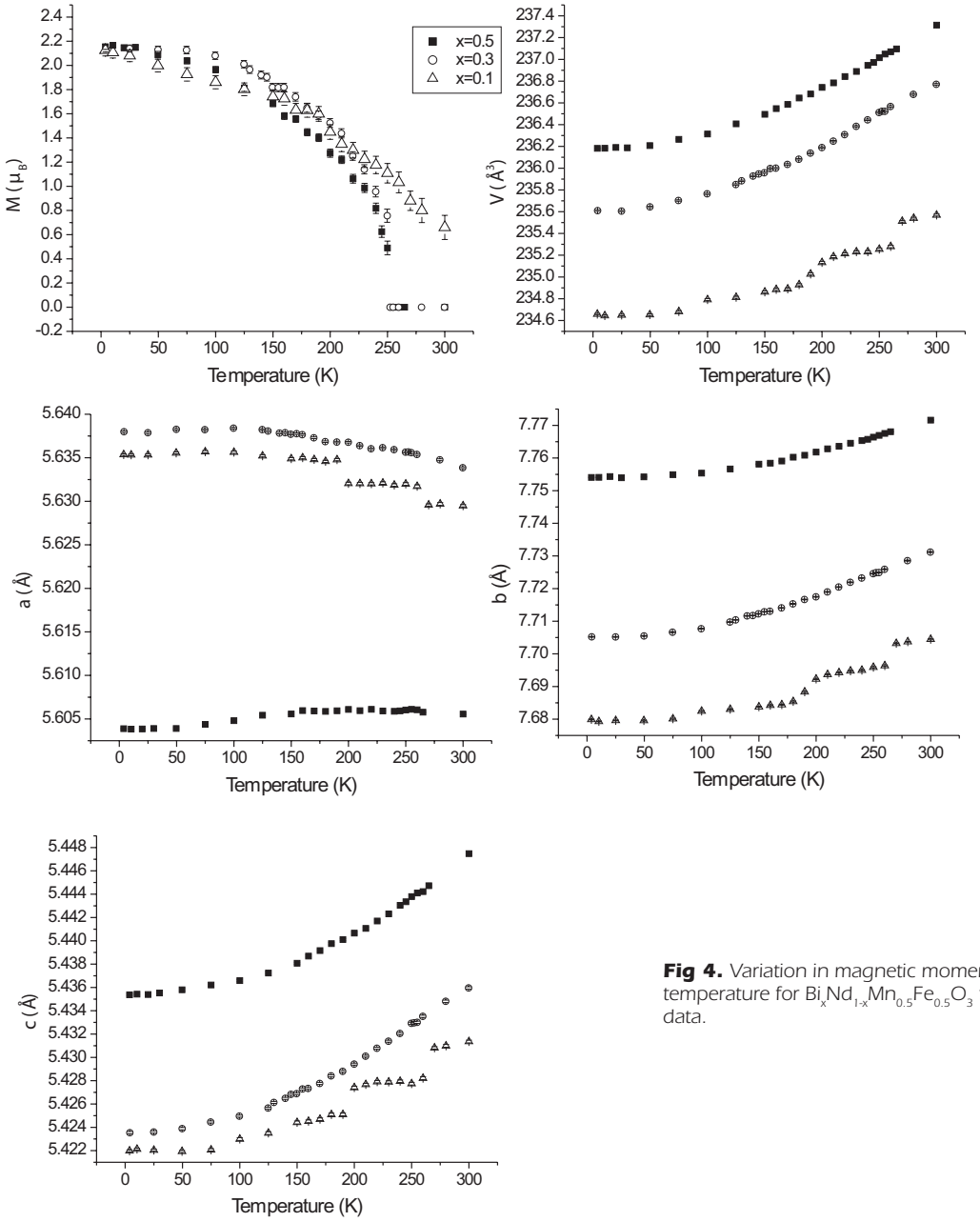


**Fig 4.** Variation in magnetic moment and lattice parameters versus temperature for $Bi_xNd_{1-x}Mn_{0.5}Fe_{0.5}O_3$ from neutron powder diffraction data.