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Neutron diffraction study of multiferroic $Tb_{0.85}Na_{0.15}MnO_{3-y}$

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Abstract

The magnetic properties and thermal evolution of $Tb_{0.85}Na_{0.15}MnO_{3-y}$ have been studied by neutron-diffraction experiments. By comparison with the $TbMnO_3$ sample, the results show not only small lattice parameters but also a reduction in correlation length (ξ). This is strongly correlated to the induced oxygen vacancies in $Tb_{0.85}Na_{0.15}MnO_{3-y}$ [$y \approx 0.15(2)$].

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Keywords: Neutron diffraction; Magnetic properties; Manganites; Multiferroic; $TbMnO_3$

1. Introduction

The spin arrangement and magnetic properties in rare-earth manganites $RMnO_3$ were studied a long time ago. The ordering temperature for the Mn ions decreases with R ionic radius, ranging from $T_N = 141$ K for La to 40 K for Tb. Moreover, the R^{3+} cations also become magnetically ordered, but at low temperature [1–5]. On the other hand, the recent discovery of very large magnetoelectric effects (ME) in the $TbMnO_3$ has reopened the field of the so-called multiferroic materials [6,7]. Since the multiferroic materials with the coexistence of (anti)ferromagnetic and (anti)ferroelectric properties are one of the best candidates to enhance the ME effects. For $TbMnO_3$, the incommensurate magnetic structure of the Mn^{3+} moments is well-known [8–13], which may be characterized by a modulation vector $(0, q_m, 0)$ that propagates along the second longest crystallographic direction *b*. q_m is incommensurate at the ordering temperature T_N (~42 K). In order to compare the differences between the magnetic properties and spin arrangement for $TbMnO_3$, this paper is to investigates the $Tb_{0.85}Na_{0.15}MnO_{3-y}$ magnetic structure and analyzes thermal evolution by using neutron powder diffraction (NPD).

2. Experimental procedures

The polycrystalline $Tb_{0.85}Na_{0.15}MnO_{3-y}$ sample was prepared by solid state reaction. Stoichiometric mixtures of Tb_4O_7, Na_2CO_3 and $MnCO_3$ were sintered in air at 1450 °C for 24 h. The high-resolution NPD patterns were collected on the BT-1 powder diffractometer at the NIST Center for Neutron Research, using a Cu (3 1 1) monochromator crystal and 15′-20′-7′ FWHM angular collimations. These diffraction patterns were analyzed using the GSAS program [14].

3. Results and discussion

The $Tb_{0.85}Na_{0.15}MnO_{3-y}$ crystal structure was refined from a NPD pattern obtained at 300 K, with $\lambda = 1.5401$ Å as shown in Fig. 1a. All the reflections were indexed in the orthorhombic space group (Pbnm) with the lattice parameters of $a = 5.2974(2)$ Å, $b = 5.7775(3)$ Å and $c = 7.4151(3)$ Å. These values are small with a recent

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report of a bulk $TbMnO_3$ sample by Blasco et al. [15]. It is well known that the ionic radius of Na^+ is ~10% larger than that of Tb^{3+}. To be noted here is that the refined of oxygen occupancy obtained for the $Tb_{0.85}Na_{0.15}MnO_{3-y}$ at 300 K is essentially oxygen stoichiometric, i.e. $y \approx 0.15(2)$. Furthermore, bond valence sum calculations [16], based on the refined bond lengths, show that the valence of Mn ions in $Tb_{0.85}Na_{0.15}MnO_{3-y}$ is trivalent. These results indicate that the decrease in the oxygen content completely counterbalanced the effect of monovalent Na^+ for trivalent Tb^{3+} cation substitution. Therefore, the reduction of the lattice parameters in our sample is thus mainly due to the occurrence of oxygen deficiencies.

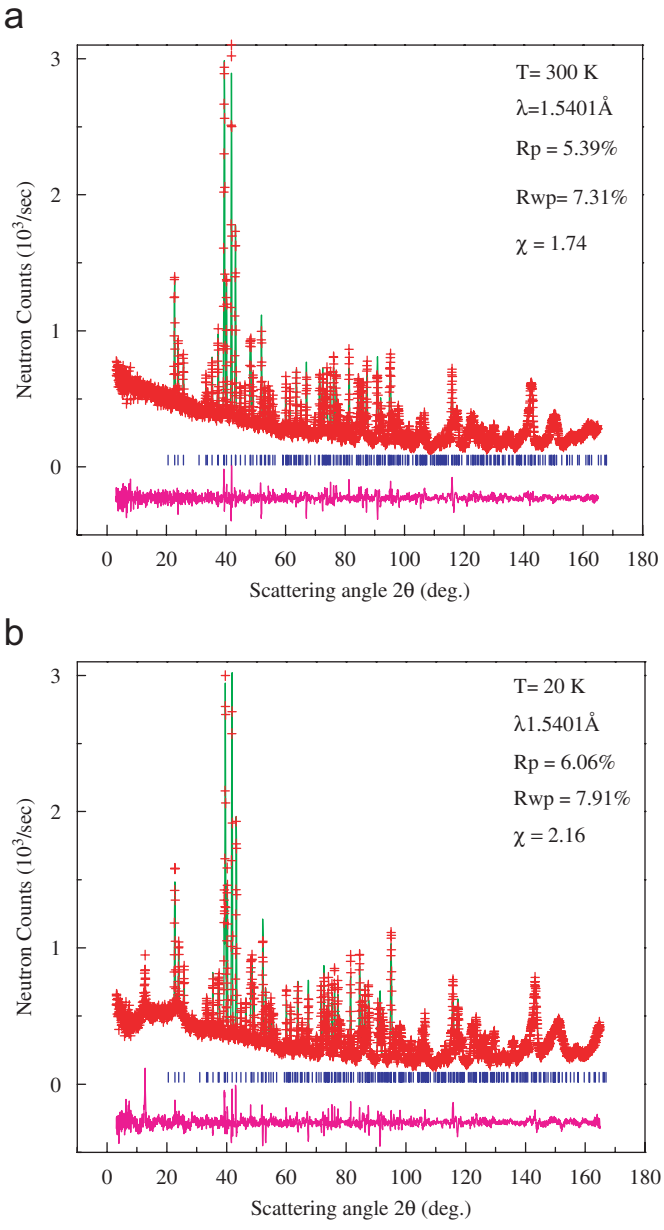

Fig. 1. Observed (crosses), calculated (solid line), and differences (bottom) NPD Rietveld profiles of $Tb_{0.85}Na_{0.15}MnO_{3-y}$ at (a) $T = 300$ K and (b) $T = 20$ K. Bragg reflections are indicated by tick mark.

Fig. 1b shows experimental, calculated and different NPD patterns for $Tb_{0.85}Na_{0.15}MnO_{3-y}$ at 20 K. Rietveld analysis afforded sufficiently low R factors, suggesting that our structure analyses were successful. At $T = 20$ K new reflections are observed at 2θ angles not allowed for the Bragg positions in the space group Pbnm. This reveals the appearance of a magnetic ordering in good agreement with that observed in the AC susceptibility measurements. Fig. 2 shows the thermal evolution of the lattice parameters and cell volume as obtained from the neutron diffractograms. The a and c unit-cell parameters present a different thermal behavior. Moreover, the cell volume smoothly decreases with decreasing temperature, and remains constant below 50 K. No phase segregation was found even with the temperature down to 3 K. The result was similar to that of a previous report [17].

The development of magnetic correlations with temperature is shown in Fig. 3. The spin arrangements for the in-plane Mn ions are also plotted in the inset. The data

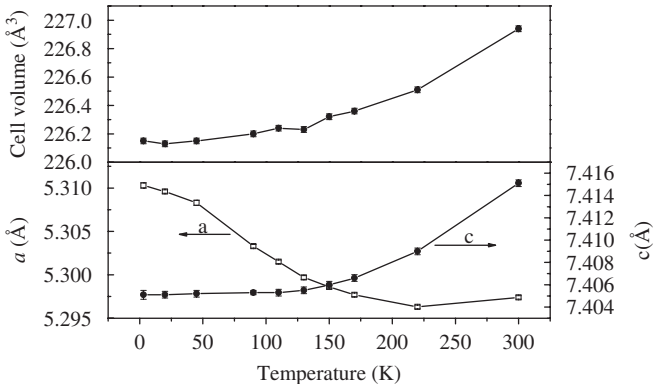

Fig. 2. Thermal evolution of the a and c lattice parameters and cell volume of $Tb_{0.85}Na_{0.15}MnO_{3-y}$.

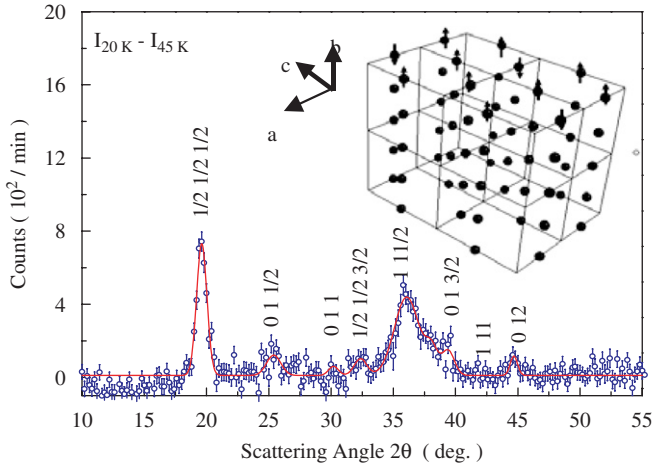

Fig. 3. Magnetic contribution as obtained by subtracting the high temperature (45 K) from the low temperature (20 K) diffraction data. The spin arrangements of the in-plane Mn ions are also plotted in the inset.

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were collected using a BT-9 triple-axis spectrometer at NIST, and the solid curves show the fits of the data to short-range scattering profiles convoluted with the Gaussian instrumental resolution. The diffraction peaks may be considered using the $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$ wave vector, with widths that are much broader than the instrumental resolution, revealing an antiferromagnetic short-range order with a correlation length of $\xi \approx 60\,\text{Å}$ for the Tb spins. By comparison with $T_{\text{Tb}} \approx 7\,\text{K}$ and $\xi \approx 140\,\text{Å}$ for the undoped $TbMnO_3$ compound [10], the reduction in ξ value can be explained by assuming the decrease in Tb content which may create more oxygen vacancies, and then weaken the correlations among the Tb ions.

4. Conclusions

In this study, we can confirm that the oxygen vacancies in $Tb_{0.85}Na_{0.15}MnO_{3-y}$ [$y \approx 0.15(2)$] play an important role in controlling the crystal structure and magnetic properties.

Acknowledgments

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