Suppression of A Site Charge Disproportionation in $Bi_{1-x}La_xNiO_3$

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Abstract

The effect of the La substitution for Bi in newly found triclinic perovskite $BiNiO_3$ was examined. The charge disproportionation of Bi ions into Bi^{3+} and Bi^{5+} was suppressed by 20 % substitution. $Bi_{0.8}La_{0.2}NiO_3$ showed a metal-insulator transition at around 300 K.

Key words: perovskite; synchrotron powder XRD; bond valence sum; charge disproportionation; $BiNiO_3$; metal-insulator transition

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1. Introduction

RNiO$_3$ perovskite (R = rare earth element and Tl) attracts much attention because of the presence of a metal-insulator (MI) transition in a systematic manner [1]. Recent neutron diffraction study revealed that the charge disproportionation ($Ni^{3+} \rightarrow Ni^{3+\delta} + Ni^{3-\delta}$) associated with the orthorhombic to monoclinic structural change causes the MI transition for RNiO$_3$ with R = Lu to Ho [2]. On the other hand, $LaNiO_3$ remains rhombohedral and metallic down to 1.5 K. It is thus expected that the replacement of La^{3+} with Bi^{3+} leads to cubic symmetry and metallicity because the ionic radius of Bi^{3+} is even larger than La^{3+}.

We have succeeded in stabilizing $BiNiO_3$ by synthesizing at a high pressure of 6 GPa [3]. Contrary to above expectation, this compound was an insulating antiferromagnet with localized $S = 1$. A precise structural analysis based on the synchrotron radiation X-ray powder diffraction (XRD) study revealed that the Bi ions were disproportionated to Bi^{3+} and Bi^{5+}, and thus, the oxidation state of Ni ion was 2+ rather than 3+.

To be reported here is the structural and physical properties of the solid solution $Bi_{1-x}La_xNiO_3$ ($0 \leq x \leq 0.5$). 20 % substitution of La for Bi suppressed the disproportionation of the A site, and made the system conducting.

2. Experiment

The high-pressure synthesis of the polycrystalline samples of $Bi_{1-x}La_xNiO_3$ ($x = 0.2$ and 0.5) were performed in the same way as $BiNiO_3$. Powder XRD data were recorded on a Rigaku RINT 2000 diffractometer using CuKα radiation. DC magnetic susceptibility measurements were performed with a Quantum Design MPMS XL SQUID magnetometer. Electrical resistivity was measured by means of standard four probe method with Quantum Design PPMS.

3. Results and discussion

Fig. 1 shows the Powder XRD patterns of $Bi_{1-x}La_xNiO_3$ with $x = 0$, 0.2 and 0.5. $BiNiO_3$ has a $\sqrt{2}a \times \sqrt{2}a \times 2a$ triclinic unit cell. On the other hand, the XRD patterns of the Bi-substituted samples were indexed as-

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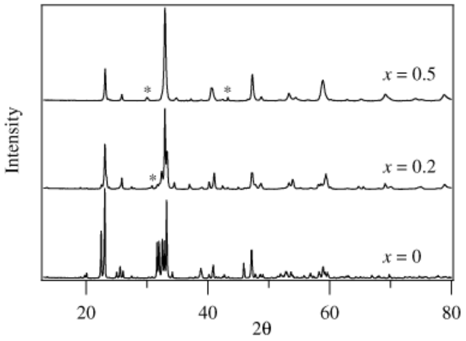

Fig. 1. Powder XRD patterns of $Bi_{1-x}La_xNiO_3$ ($x = 0$, 0.2 and 0.5). The asterisks indicate the peaks from impurity phases.

suming orthorhombic symmetry. The most significant difference was found in the unit cell volumes at room temperature. As shown in Fig. 2, there was a 3 % volume jump between $x = 0$ and 0.2 suggesting the change in the oxidation state of Ni from 2+ to 3+.

This assertion was supported by the inverse magnetic susceptibility data shown in Fig. 3. All the samples showed antiferromagnetic transitions with spin canting at around 300 K, but the slope above T_N changed drastically between $x = 0$ and 0.2. The slope of $x = 0$ sample was corresponding to a $S = 1$ (Ni^{2+}) system while those for $x = 0.2$ and 0.5 samples were consistent with $S = 1/2$ (Ni^{3+}) ones. Since the divalent nature of Ni ion in $BiNiO_3$ is the consequence of disproportionation of Bi^{3+} and Bi^{5+} , these results mean that the disproportionation was suppressed by the La substitution for Bi.

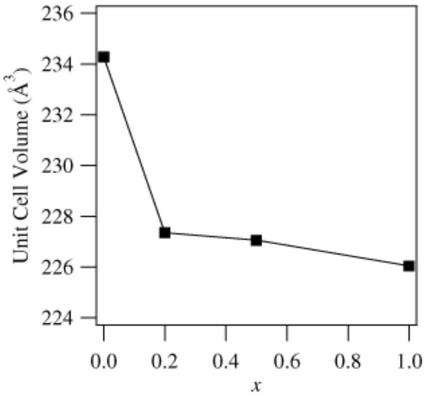

Fig. 2. The unit cell volume of $Bi_{1-x}La_xNiO_3$. The datum for $LaNiO_3$ is taken from ref. [4] and is multiplied by two thirds.

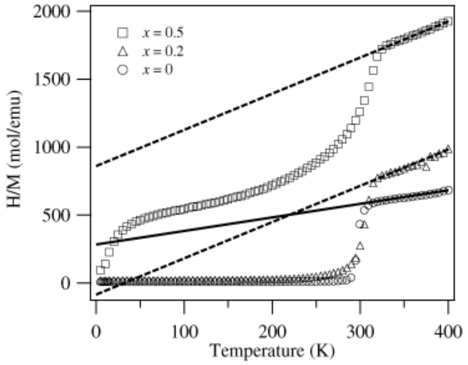

Fig. 3. Temperature dependences of the inverse molar magnetic susceptibility for $Bi_{1-x}La_xNiO_3$. The solid and dashed lines indicate the slope for $S = 1$ and 1/2 systems, respectively.

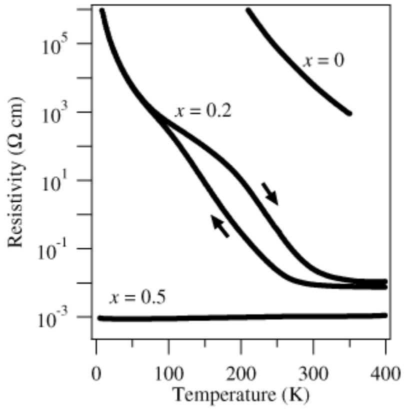

Fig. 4. Temperature dependences of the resistivity of $Bi_{1-x}La_xNiO_3$ ($x = 0$, 0.2 and 0.5)

As results, $x = 0.2$ and 0.5 samples showed metallic behaviors at room temperature as shown in Fig. 4. $Bi_{0.5}La_{0.5}NiO_3$ was metallic down to 5 K as $LaNiO_3$, while $Bi_{0.8}La_{0.2}NiO_3$ exhibited a broad metal-insulator transition below 300 K. The transition temperature was close to T_N, but it was not clear whether the MI transition was caused by the magnetic ordering or not. Resistivity data measured in a magnetic field of 1 T did not show significant change. Another possibility is the structural transition. The large hysteresis in the resistivity data is indicative of the first order transition, but there are two possible scenarios, one is the disproportionation of A site as in $BiNiO_3$ and the other is $Ni^{3+} \rightarrow Ni^{3+\delta} + Ni^{3-\delta}$ as in $YNiO_3$. Detailed structural analysis will clarify the mechanism of the MI transition in this system.

References

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