Structure and Physical Properties of Perovskite $Bi_{0.8}Pb_{0.2}NiO_3$ in Unusual Valence State $A^{4+}B^{2+}O_3$

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The effects of Pb substitution for Bi on structure and physical properties of $BiNiO_3$ were studied. The solid solutions $Bi_{1-x}Pb_xNiO_3$ ($x = 0.1$, 0.2) were synthesized under high pressures of 8−10 GPa. We have found that $Bi_{1-x}Pb_xNiO_3$ changes from triclinic perovskites with $x \leq 0.1$ to an orthorhombic perovskite with $x = 0.2$. Structural analysis on the basis of synchrotron X-ray powder diffraction data for the composition with $x = 0.2$ revealed an unusual valence state $(Bi_{0.8}Pb_{0.2})^{4+}Ni^{2+}O_3$ stabilized in a heavily distorted $GdFeO_3$-type structure. Although the charge disproportionation of Bi in $BiNiO_3$ was suppressed by 20% Pb substitution, the substituted compound remained semiconducting with an antiferromagnetic transition at 340 K. The exotic structural features found in the solid solutions $Bi_{1-x}Pb_xNiO_3$ demonstrate strong covalency of the (Bi, Pb)−O bonds and the robustness of Ni^{2+}.

1. Introduction

Perovskite-type 3d-transition-metal oxides denoted as ABO_3 have attractive electronic properties, exemplified by ferroelectricity, ferromagnetism, and superconductivity.[1] In general, although the network of corner-shared BO_6 octahedra (B: 3d transition metals) is in charge of these electronic functions, they can be controlled by substitution of the A-site ions (A: lanthanides, typically), changing crystal symmetry and working as a charge reservoir.[2] According to the calculations of Madelung potential energy for perovskite oxides, the B-site ions favor a higher-valence state than the A-site ions, so that three kinds of valence states, $A^{3+}B^{3+}O_3$, $A^{2+}B^{4+}O_3$, and $A^{+}B^{5+}O_3$, are stabilized in nature.[3]

Recently, an exceptional compound, $BiNiO_3$, has been found to have a valence state, $Bi^{3+}{}_{0.5}Bi^{5+}{}_{0.5}Ni^{2+}O_3$.[4] This compound crystallizes in a triclinically distorted perovskite and shows insulating behavior. The A-site charge disproportionation (CD) can be suppressed by applying an external pressure of several GPa or substituting A-site partially with La, which turns the system into an orthorhombic and metallic phase.[5,6] According to the bond valence calculations and the analyses of Ni 2p X-ray absorption spectra for the orthorhombic phase of $Bi_{1-x}La_xNiO_3$,[7] the valence of Ni ions is neither +2 nor +3 but in between them, reflecting the nature of charge fluctuation between the A-site and the B-site ions. Then, the question is whether the Bi ions occupying the A-site is conducting or not in the orthorhombic, metallic phase. One may expect that Pb^{4+} substitution for the A-site of $BiNiO_3$ suppresses the A-site CD and leads to $A^{4+}B^{2+}O_3$-type perovskite, of which the A−O sublattice is conductive.

In this paper, we report on syntheses, structure, and physical properties of $Bi_{1-x}Pb_xNiO_3$ ($x = 0.1$, 0.2). Although the A-site CD is suppressed by 20% Pb substitution, the system remains semiconducting with an antiferromagnetic transition at 340 K. The structure analyses together with the magnetic and resistivity measurements allow us to propose an unusual valence state $(Bi_{0.8}Pb_{0.2})^{4+}Ni^{2+}O_3$, which is manifestation of strong covalency of the (Bi, Pb)−O bonds and the robustness of Ni^{2+}.

2. Experimental Section

Polycrystalline samples of $Bi_{1-x}Pb_xNiO_3$ ($x = 0.1$, 0.2) were prepared with a conventional cubic anvil-type HP apparatus. The starting materials, Bi_2O_3, PbO, and Ni, in stoichiometric amounts were dissolved in nitric acid and heated in air at 650−700 °C for 6 h. The sample mixed with $KClO_4$ (20 wt %) was sealed in a gold capsule ($\phi 3 \times 5$ mm) and was subjected to a treatment at 1000 °C and at 8 ($x = 0.1$) to 10 ($x = 0.2$) GPa for 20 min, followed by quenching to room temperature. Note that the heating rate for the HP syntheses of $Bi_{1-x}Pb_xNiO_3$ should be as high as possible to suppress the formation of an unidentified secondary phase. After being taken out of the capsule, the product was crushed and washed with distilled water to remove KCl. The polycrystalline sample used for resistivity measurements was pressed to be a dense pellet at a high pressure of 4 GPa at room temperature. Electrical resistivities were measured by a four-probe method using a PPMS (Quantum Design). DC magnetic susceptibility were measured with a MPMS SQUID magnetometer (Quantum Design) in an external magnetic field of 0.1 T.

Powder XRD data for phase identification were recorded on a Rigaku RINT 2500 diffractometer using Cu $K\alpha$ radiation. Syn-

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(1) Goodenough, J. B.; Zhou, J.-S. *Chem. Mater.* **1998**, *10*, 2980−2993.
(2) Attfield, J. P. *Chem. Mater.* **1998**, *10*, 3239−3248.
(3) Yoshimura, M.; Nakamura, T.; Sata, T. *Bull. Tokyo Inst. Technol.* **1974**, *120*, 13−27.
(4) Ishiwata, S.; Azuma, M.; Takano, M.; Nishibori, E.; Takata, M.; Sakata, M.; Kato, K. *J. Mater. Chem.* **2002**, *12*, 3733−3737.
(5) Ishiwata, S.; Azuma, M.; Takano, M. *Solid State Ionics* **2004**, *172*, 569−571.
(6) Ishiwata, S.; Azuma, M.; Hanawa, M.; Moritomo, Y.; Ohishi, Y.; Kato, K.; Takata, M.; Nishibori, E.; Sakata, M.; Terasaki, I.; Takano, M. *Phys. Rev. B* **2005**, *72*, 045104.
(7) Wadati, H.; Takizawa, M.; Tran, T. T.; Tanaka, K. Mizokawa, T.; Fujimori, A.; Chikamatsu, A.; Kumigashira, H.; Oshima, M.; Ishiwata, S.; Azuma, M.; Takana, M. *Phys. Rev. B* **2005**, *72*, 155103.

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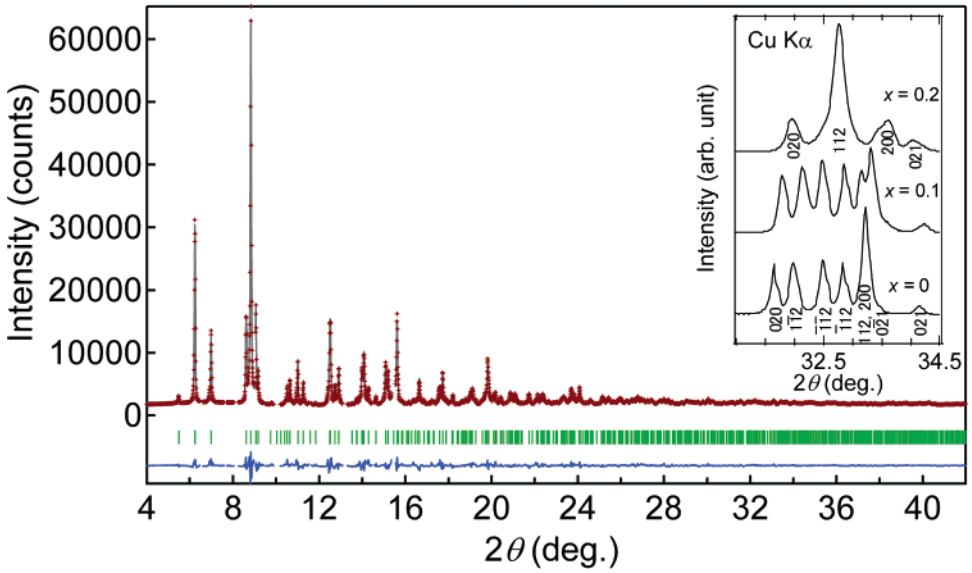

Figure 1. Measured (+), calculated (line), and differential (bottom line) XRD patterns of $Bi_{0.8}Pb_{0.2}NiO_3$ ($\lambda = 0.42091$ Å). The ticks indicate the positions of the reflections. Inset: XRD patterns of $Bi_{1-x}Pb_xNiO_3$ ($x = 0$, 0.1, 0.2) with indices measured with Cu $K\alpha$ radiation.

Table 1. Space Group, Lattice Parameters, and Cell Volumes of $Bi_{1-x}Pb_xNiO_3$ ($x = 0$, 0.1, 0.2)

x	S.G.	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)	V (Å^3)
0	$P\bar{1}$	5.3852(2)	5.6498(2)	7.7078(3)	91.953(1)	89.810(1)	91.541(1)	234.29(1)
0.1	$P\bar{1}$	5.3653(5)	5.6207(5)	7.7194(6)	91.712(4)	89.927(4)	91.091(4)	232.64(3)
0.2	*Pbnm*	5.3174(4)	5.5917(4)	7.7280(5)				229.77(3)

chrotron X-ray diffraction (SXRD) data of $Bi_{0.8}Pb_{0.2}NiO_3$ at room temperature were collected on an imaging plate (IP) using a large Debye−Scherrer camera installed at BL02B2 of SPring-8.[8] The granularity of the polycrystalline sample was homogenized to 2−3 μm in diameter by the precipitation method. The as-prepared sample was sealed into a glass capillary with a internal diameter of 0.1 mm. The wavelength of 0.42091 Å was adopted as an incident beam. The data collected in 0.01° step were analyzed by the Rietveld method using a Rietan 2000 program.[9] Unidentified peaks from tiny amount of impurities, which are sometimes found in the products of HP syntheses for Bi-based oxides, were excluded during the refinements.

3. Results and Discussions

The solid solutions $Bi_{1-x}Pb_xNiO_3$ undergo a structural transition from the triclinic to the $GdFeO_3$-type perovskite upon increasing x from 0.1 to 0.2 (inset of Figure 1). The XRD pattern of $Bi_{0.8}Pb_{0.2}NiO_3$ was indexed with an orthorhombic cell of 5.32 × 5.59 × 7.73 Å. The XRD pattern together with the refined profile calculated on the basis of space group of *Pbnm* (No. 62) are shown in Figure 1. The reflection condition for the indexed peaks affords two possible space group, $Pbn2_1$ (No. 33) and *Pbnm* (No.62). Recently, a newly synthesized perovskite $BiInO_3$ was found to crystallize in space group $Pbn2_1$.[10] However, attempts to fit the present data with $Pbn2_1$ have resulted in no significant improvement of the refinements. Space group and lattice parameters of $Bi_{1-x}Pb_xNiO_3$ are summarized in Table 1. Although 10% Pb substitution relieves the triclinic distortion to some degree, it is not enough to change the system into the $GdFeO_3$-type perovskite, whereas the same ratio of La substitution for Bi is enough to do so. This difference signifies that the Pb substitution is less effective in disturbing the charge disproportionated state, $Bi_{0.5}^{3+}Bi_{0.5}^{5+}Ni^{2+}O_3$.

Table 2. Refined Structural Parameters of $Bi_{0.8}Pb_{0.2}NiO_3$ in the Space Group *Pbnm* (No. 62)[a]

atom	site	occ.	x	y	z	B (Å^2)
Bi	4*c*	0.8	0.9843(3)	0.0535(2)	1/4	0.96(4)
Pb	4*c*	0.2	0.9843(3)	0.0535(2)	1/4	0.96(4)
Ni	4*b*	1	1/2	0	0	0.90(7)
O1	4*c*	1	0.118(3)	0.385(3)	1/4	1.7(3)
O2	8*d*	1	0.717(3)	0.304(3)	0.076(2)	1.7(3)

[a] $a = 5.3174(4)$ Å, $b = 5.5917(4)$ Å, $c = 7.7280(5)$ Å, $V = 229.77(3)$ Å^3, $Z = 4$, $D = 9.11$ g/cm^3; $R_{wp} = 5.34\%$, $R_p = 3.73\%$, $R_I = 1.43\%$, $S = 2.70$.

The atomic coordinates, the equivalent isotropic thermal factors, and the reliability factors of $Bi_{0.8}Pb_{0.2}NiO_3$ are listed in Table 2, and the selected bond distances and angles are listed in Table 3. By applying the Brown's bond valence model[11] ($s_i = \exp[(r_0 - r_i)/B]$, $B = 0.37$, $r_0 = 1.654$ for Ni^{2+}−O) to these data, the valence of Ni was calculated to be +1.99. Given the stoichiometric composition and the divalent state of Ni ions in $Bi_{0.8}Pb_{0.2}NiO_3$, the tetravalent state is most likely for the A-site ions. As it is tricky to estimate the valence for the A-site ion, we examined each r_0, 2.09, 2.06, 2.112, and 2.042 for Bi^{3+}−O, Bi^{5+}−O, Pb^{2+}−O, and Pb^{4+}−O, yielding bond valences of +4.56, +4.21,

(8) Nishibori, E.; Takata, M.; Kato, K.; Sakata, M.; Kubota, Y.; Aoyagi, S.; Kuroiwa, Y. ; Yamakata, M.; Ikeda, N. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2001**, *467*−*468*, 1045−1048.
(9) Izumi, F.; Ikeda, T. *Mater. Sci. Forum* **2000**, *198*, 321−324.
(10) Belik, A. A.; Stefanovich, S. Y.; Lazoryak, B. I.; Takayama-Muromachi, E. *Chem. Mater.* **2006**, *18*, 1964−1968.
(11) Brese, N. E.; O'Keeffe, M. *Acta. Crystallogr., Sect. B* **1991**, *47*, 192−197.

Table 3. Selected Bond Distances and Bond Angles of $Bi_{0.8}Pb_{0.2}NiO_3$

atoms	bond length (Å)	atoms	bond length (Å)	atoms	bond angle (deg)
A−O1	1.985(18)	Ni−O2 (× 2)	1.950(14)	O1−Ni−O2	77.2(3)
A−O2 (× 2)	2.216(12)	Ni−O1 (× 2)	2.131(7)	O1−Ni−O2	81.3(6)
A−O1	2.316(16)	Ni−O2 (× 2)	2.137(15)	O2−Ni−O2	87.0(2)
A−O2 (× 2)	2.408(16)	average Ni−O	2.07	Ni−O1−Ni (× 2)	130.1(9)
A−O1 (× 2)	2.915(16)	average $<A-O>_6$	2.26	Ni−O2−Ni (× 4)	141.4(6)
A−O1	3.338(16)				

+4.84, and +4.01, respectively. These calculations allow us to presume the plausible valence state to be $(Bi_{0.8}Pb_{0.2})^{4+}$-$Ni^{2+}O_3$ rather than $(Bi_{0.8}Pb_{0.2})^{3+}Ni^{3+}O_3$. The presumption that Pb ions at the A-site are tetravalent is quite reasonable because the Pb^{4+} substitution, which keeps the charge distribution of $A^{4+}B^{2+}O_3$, is expected to be less effective for suppression of the A-site CD compared to the La^{3+} substitution.

Figure 2 shows that the crystal structure of $Bi_{0.8}Pb_{0.2}NiO_3$. NiO_6 octahedra are distorted (O−Ni−O bond angles are significantly deviated from 90° as seen in Table 3) and heavily tilted from the regular orientation (Figure 2a). The averaged Ni−O−Ni angle is as small as 137.6°, which is close to that of $BiNiO_3$, 136.9°, and that of $BiInO_3$, 139.5°.

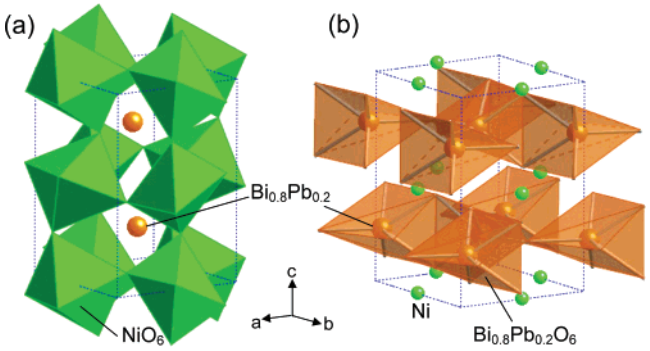

Figure 2. Schematic crystal structure of $Bi_{0.8}Pb_{0.2}NiO_3$: (a) linkage of NiO_6 octahedra, and (b) linkage of AO_6 (A = $Bi_{0.8}Pb_{0.2}$) trigonal prisms.

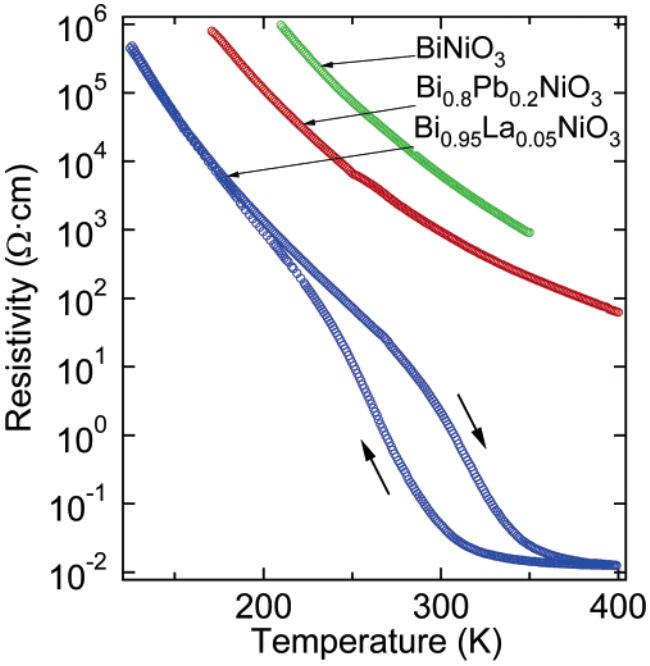

Figure 3. Temperature dependence of resistivity for $BiNiO_3$, $Bi_{0.8}Pb_{0.2}NiO_3$, and $Bi_{0.95}La_{0.05}NiO_3$.

The coordination number for the A-site ions in a perovskite structure tends to decrease as the degree of structural distortion increases. It is 12 for the simple cubic perovskite, whereas it is commonly 8 for the $GdFeO_3$-type perovskite. However, because of a strong covalent character, the A-site ion of $Bi_{0.8}Pb_{0.2}NiO_3$ is coordinated by only six oxygen ions (1.99−2.41 Å) as well as $BiNiO_3$ but in a different fashion. As illustrated in Figure 2b, the distorted trigonal prisms, AO_6, share two edges and two corners with the adjacent ones to form a bidimensional lattice normal to the *c*-axis. Such a peculiar A−O sublattice has also been found in $BiInO_3$, where distorted BiO_6 octahedra are linked by a corner to form a three-dimensional network. Thus, the heavy distortion in these Bi-based perovskites is independent of the A-site CD and should stem from the strong covalency of (Bi, Pb)−O bonds and the steric effect of $6s^2$ lone pairs.

Next, we discuss Pb-substitution effects on the physical properties of $BiNiO_3$. Figure 3 shows resistivity of $Bi_{0.8}Pb_{0.2}$-NiO_3, $Bi_{0.95}La_{0.05}NiO_3$, and $BiNiO_3$ as a function of temperature. The Pb substitution for Bi suppressed the A-site CD, but by contrast with the La substitution, the system remains semiconducting. $Bi_{0.95}La_{0.05}NiO_3$ becomes metallic as the A-site CD is suppressed in the orthorhombic phase above approximately 350 K, whereas $Bi_{0.8}Pb_{0.2}NiO_3$ is semiconducting despite the absence of the A-site CD. Thus, the presence of holes on the $Ni^{(2+\delta)+}$−O sublattice should be responsible for metallicity in $Bi_{0.95}La_{0.05}NiO_3$. The thermal activation energy of $Bi_{0.8}Pb_{0.2}NiO_3$ was estimated to be 537 meV, slightly smaller than that of $BiNiO_3$, 675 meV. Here, we give attention to a metal-semiconductor transition in $BaBi_{1-x}Pb_xO_3$ at $x \approx 0.65$.[12] In the range $0 \leq x < 0.65$, $BaBi_{1-x}Pb_xO_3$ has a gap introduced by a local charge-density-wave (CDW) instability of Bi ions disproportionated into Bi^{3+} and Bi^{5+}.[13] Therefore, increments of Pb concentration or applying external pressure may eventually lead $Bi_{1-x}Pb_xNiO_3$ to the novel A-site conducting perovskite.

As shown in Figure 4, the Neel temperature T_N of $Bi_{1-x}Pb_xNiO_3$ increases with increasing *x*. Consistent with the bond valence calculations confirming the divalent nature of Ni ions, the inverse molar magnetic susceptibility in the Curie−Weiss-like paramagnetic region indicates the presence of antiferromagnetically interacting spins of $S = 1$ (Ni^{2+}). Note that the exchange interaction in the Heisenberg model is proportional to t^2/U, where *t* and *U* denote the intersite transfer integral and the on-site Coulomb repulsion, so that the increment of T_N corresponds to an increment of the

(12) Sleight, A. W.; Gillson, J. L.; Bierstadt, P. E. *Solid State Commun.* **1975**, *17*, 27−28.
(13) Tajima, S.; Uchida, S.; Masaki, A.; Takagi, H.; Kitazawa, K.; Tanaka, S. *Phys. Rev. B* **1987**, *35*, 696−703.

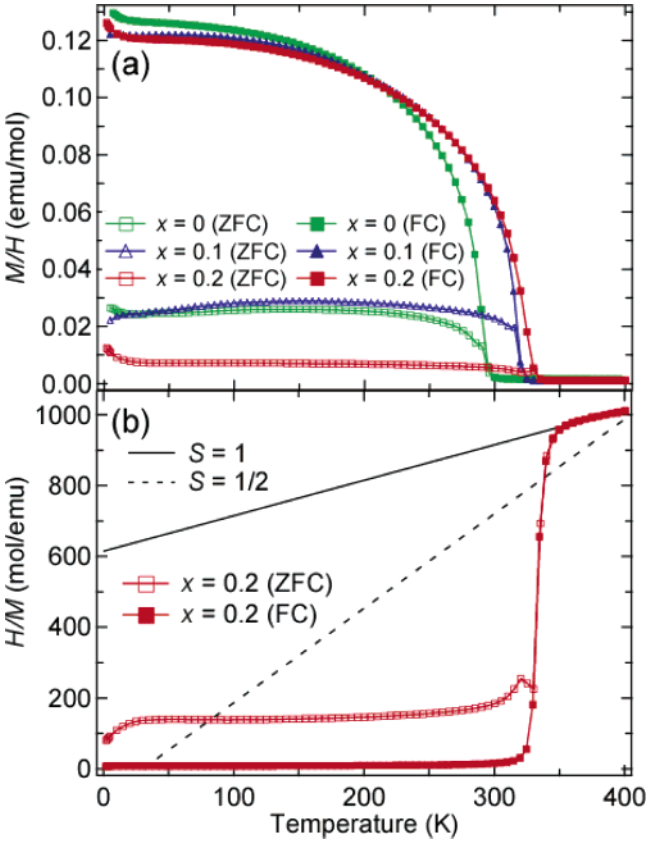

Figure 4. Temperature dependence of (a) molar magnetic susceptibility for $Bi_{1-x}Pb_xNiO_3$ (x = 0, 0.1, 0.2) and (b) inverse molar magnetic susceptibility for $Bi_{0.8}Pb_{0.2}NiO_3$, measured in an external magnetic field of 0.1 T on heating after zero-field cooling (ZFC) and then on cooling (FC). The solid and broken lines in part b correspond to the slopes expected for $S = 1$ and $S = 1/2$ systems, respectively.

transfer integral. Because the bond angle of Ni−O−Ni is almost the same, the transfer integral derived from a path of Ni−O−A−O−Ni may be enhanced by the doping of Pb^{4+}. The magnetization curves in Figure 5 clearly shows weak ferromagnetic moments (~0.02 μ_B/mol at 5 K) presumably induced by a Dzyaloshinsky−Moriya (D−M) interaction inherent to the heavily distorted structure. The temperature-dependent magnetic susceptibility and the $M-H$ curves showed hysteretic behavior as observed in $BiNiO_3$. The initial magnetization curves show different behavior from the other curves forming $M-H$ hysteresis loops, which can be explained by the rotation of magnetic domains having weak ferromagnetic moments. Neutron diffraction studies are worth future consideration in studying the magnetism of this system.

In summary, we synthesized the solid solutions $Bi_{1-x}Pb_xNiO_3$ (x = 0.1, 0.2) under a high pressure of 8−10 GPa and studied its structure and physical properties.

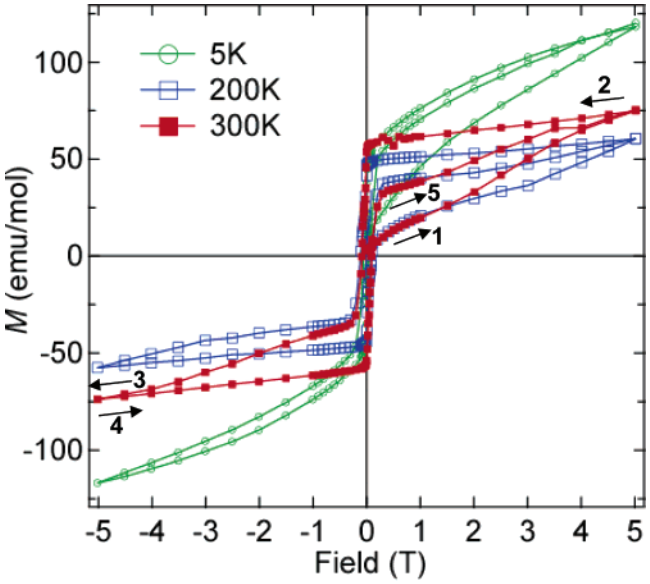

Figure 5. Magnetization curves of $Bi_{0.8}Pb_{0.2}NiO_3$ measured at 5, 200, and 300 K. The sequential numbers with arrows indicate the run of the measurement at 300 K.

Structure analysis on the basis of the synchrotron X-ray diffraction measurement revealed that the A-site CD in $BiNiO_3$ was suppressed by the 20% substitution with Pb^{4+} in a following manner, $Bi^{3+}{}_{0.5}Bi^{5+}{}_{0.5}Ni^{2+}O_3 \rightarrow (Bi_{0.8}Pb_{0.2})^{4+}$-$Ni^{2+}O_3$. $Bi_{0.8}Pb_{0.2}NiO_3$ crystallizes in the $GdFeO_3$-type structure having the novel valence state, $A^{4+}B^{2+}O_3$. On the other hand, $Bi_{0.9}Pb_{0.1}NiO_3$ remains triclinically distorted, which suggests that the effect of Pb^{4+} substitution on the A-site CD is rather mild compared to that of La^{3+} substitution. These results manifest the highly covalent (Bi, Pb)−O bonds, in addition to a great stability of the electronic state of Ni^{2+}. The Curie−Weiss fit for the paramagnetic susceptibility was consistent with the presence of robust Ni^{2+} giving rise to a localized moment of $S = 1$. Although the magnetism and the resistivity of $Bi_{0.8}Pb_{0.2}NiO_3$ are similar to those of $BiNiO_3$, the Neel ordering temperature of the former is higher by 40 K than the latter, which can be associated with the doping of Pb^{4+} into the A−O sublattice. The $A^{4+}B^{2+}O_3$-type perovskites, $Bi_{1-x}Pb_xNiO_3$, open up a new electronic state of perovskite oxides.

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