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Atomic disorder of $Li_{0.5}Ni_{0.5}O$ thin films caused by Li doping: estimation from X-ray Debye–Waller factors

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Cubic type room-temperature (RT) epitaxial $Li_{0.5}Ni_{0.5}O$ and NiO thin films with [111] orientation grown on ultra-smooth sapphire (0001) substrates were examined using synchrotron-based thin-film X-ray diffraction. The $1\bar{1}1$ and $2\bar{2}2$ rocking curves including six respective equivalent reflections of the $Li_{0.5}Ni_{0.5}O$ and NiO thin films were recorded. The RT B_1 factor, which appears in the Debye–Waller factor, of a cubic $Li_{0.5}Ni_{0.5}O$ thin film was estimated to be 1.8 (4) Å^2 from its $1\bar{1}1$ and $2\bar{2}2$ reflections, even though the Debye model was originally derived on the basis of one cubic element. The corresponding Debye temperature is 281 (39) K. Furthermore, the B_2 factor in the pseudo-Debye–Waller factor is proposed. This parameter, which is evaluated using one reflection, was also determined for the $Li_{0.5}Ni_{0.5}O$ thin film by treating $Li_{0.5}Ni_{0.5}O$ and NiO as ideal NaCl crystal structures. A structural parameter for the atomic disorder is introduced and evaluated. This parameter includes the combined effects of thermal vibration, interstitial atoms and defects caused by Li doping using the two Debye–Waller factors.

1. Introduction

$Li_xNi_{1-x}O$ has attracted considerable attention recently as a potential material for high-performance electrochromic devices (Moulki *et al.*, 2012), UV detectors (Ohta *et al.*, 2003) and gas sensors (Garduno-Wilches & Alonso, 2013). Recently, cubic type NiO thin films with (111) orientation containing large amounts of Li (up to 50 mol%) were epitaxically grown on ultra-smooth sapphire (0001) substrates by room-temperature (RT) pulsed laser deposition (Shiraishi *et al.*, 2010; Yang *et al.*, 2014). The ultra-smooth sapphire substrate used in this work has an atomic 'step and terrace' structure on its surface, which consists of atomically flat terraces comprising single oxygen layers separated by periodic atomic steps with 0.22 nm height corresponding to the oxygen layer spacing along the *c* axis. These films could be grown even though bulk NiO containing over 30 mol% Li undergoes a phase transformation from the cubic to rhombohedral structure (Goodenough *et al.*, 1958).

The Debye temperature is an important characteristic structural parameter of a solid and describes the dynamic motions of atoms in the material. A number of physical parameters such as mean-square atomic displacement (Herbstein, 1961) and elastic constant (Gazzara & Middleton, 1964) depend on the Debye temperature of a solid. Therefore,

Li or Ni

Li
Ni
O
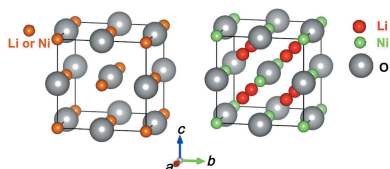
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it is very important to determine the Debye temperature of $Li_xNi_{1-x}O$ in order to understand its physical properties, such as the change of heat capacity caused by Li doping, and develop related electronic devices. X-ray diffraction is a valuable method to study thin films and other epitaxial layer materials. The changes of the lattice constant and crystal quality caused by doping are frequently evaluated using this method (Dutta *et al.*, 2010; Palatnikov *et al.*, 2006). However, the effect of atomic disorder caused by doping elements on the X-ray diffraction intensity has seldom been estimated (Sakata & Hashizume, 1997). In this study, we attempted to quantitatively analyze the effect of atomic disorder caused by Li doping on the X-ray diffraction intensity of an $Li_{0.5}Ni_{0.5}O$ thin film.

2. History of Debye temperature estimation by X-ray diffraction

Originally, the Debye temperature was determined using X-ray diffraction and was strictly limited to monoatomic cubic crystals. The integrated intensity, I, from a cubic sample can be expressed as (James, 1962) $I = KL_p^{hkl}|F|^2D$, where K is a constant, which is a normalized factor depending on the experimental arrangement, L_p^{hkl} is the Lorentz–polarization factor $(1 + \cos^2 2\theta_{hkl})/(2\sin^2\theta_{hkl}\cos\theta_{hkl})$, h, k and l are the Miller indices of the diffraction plane, θ is the Bragg diffraction angle, $|F|$ is the modulus of the structure factor, and D is the Debye–Waller factor, expressed as $\exp(-2B\sin^2\theta/\lambda^2)$. Here (James, 1962)

$$B = 8\pi^2\overline{u^2} = \frac{24\hbar^2\pi^2 T}{mk_B\theta_M^2}\left[\Phi(x) + \frac{x}{4}\right] \quad (1)$$

and

$$\Phi(x) = \frac{1}{x}\int_0^x \frac{y}{\exp(y)-1}\,dy, \quad x = \theta_M/T. \quad (2)$$

$\overline{u^2}$ is the mean-square displacement of atoms from the sites of the average lattice of the solid solution. m is the mass of the atom, k_B is the Boltzmann constant, $\hbar$ is Planck's constant divided by 2π, θ_M is the Debye temperature and T is the experimental temperature.

Later, the Debye theory was extended to apply to binary alloys, such as KCl and NaCl, whose specific heats can be fairly well described by the Debye–Waller formula with an appropriate value of the characteristic temperature (James, 1962). The structure factor for binary alloys is formally written as (Murakami, 1953)

$$F(hkl) = r_Af_A\exp[2i\pi(hx_A + ky_A + lz_A)]\exp(-B_A\sin^2\theta/\lambda^2)$$
$$+ r_Bf_B\exp[2i\pi(hx_B + ky_B + lz_B)]\exp(-B_B\sin^2\theta/\lambda^2). \quad (3)$$

Here f is the atomic scattering factor, x, y, z are the atomic positions in the unit cell, and the subscripts A and B refer to the two components of the alloy. r_A and r_B are the atomic fractions of A and B, respectively. To perform a simple approximation (Kulkarni & Bichile, 1977; Wathore & Kulk-

arni, 1980; Pathak & Trivedi, 1973), we let $B_A = B_B = \overline{B}$, and in equation (1) use $\overline{m} = r_Am_A + r_Bm_B$. This approximation allows a quasi-Debye temperature to be obtained. The experimental results summarized by Lonsdale (1948) are in reasonable agreement with this approximation.

3. Introduction of a structure parameter

The Debye temperature has been evaluated from X-ray intensities not only at different temperatures for a Bragg peak (Herbstein, 1961) but also from different reflections at a given temperature (Herbstein, 1961; Kulkarni & Bichile, 1977). Here, a real Debye–Waller factor D_1 for an $Li_{0.5}Ni_{0.5}O$ thin film was obtained by X-ray diffraction using two different reflections, $1\bar{1}1$ and $2\bar{2}2$, with the assumption that the rock-salt lattice is a simple cubic structure composed of one kind of atom and the Li atoms occupy Ni substitutional positions without any atomic disorder. We also assume that the thermal disorder contributes to the ratio of the diffracted intensities between the $1\bar{1}1$ and $2\bar{2}2$ reflections for simplicity. Second, a pseudo-Debye–Waller factor D_2 for the $Li_{0.5}Ni_{0.5}O$ thin film was obtained from the X-ray $1\bar{1}1$ intensity ratio between $Li_{0.5}Ni_{0.5}O$ and NiO. Finally, we introduce an atomic disorder parameter $\exp(\delta)$ ($\delta \leq 0$), including the combined effects of thermal vibration, interstitial atoms and defects expressed using D_1, D_2 and the reported NiO Debye temperature (Freer, 1981). This term is required because the positions of atoms are changed by Li doping. This process is outlined in Fig. 1.

4. Samples and experiment

$Li_xNi_{1-x}O$ thin films were epitaxically grown on ultra-smooth sapphire (0001) substrates (Yoshimoto *et al.*, 1995) by RT pulsed laser deposition. Details of the deposition conditions have been reported elsewhere (Shiraishi *et al.*, 2010; Yang *et al.*, 2014). The compositions of NiO thin films containing large amounts of Li grown at RT were determined using inductively coupled plasma atomic emission spectrometry (Shimadzu ICPS-8100). The lithium contents x in the $Li_xNi_{1-x}O$ samples were 0 and 0.5. The periodicities of the intensity oscillations appearing in the X-ray reflectivity curves revealed that the thicknesses t of the NiO and $Li_{0.5}Ni_{0.5}O$ epitaxial thin films were 400 (21) and 231 (6) Å, respectively.

X-ray diffraction measurements were performed with a six-axis diffractometer at the National Institute for Materials
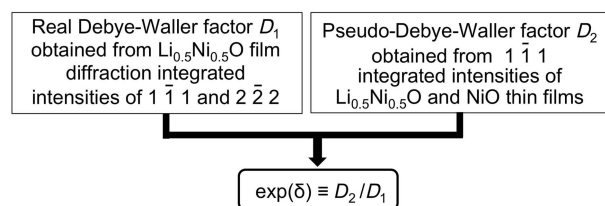

Figure 1
The definition of a structure parameter [$\exp(\delta)$] to describe the effect of atomic disorder caused by Li doping on the X-ray diffraction intensity of an $Li_{0.5}Ni_{0.5}O$ thin film.

Science (NIMS) beamline BL15XU, SPring-8. The wavelength used was 1.000 Å.

5. Results and discussion

5.1. Crystal structure

The crystallographic epitaxy between the $Li_xNi_{1-x}O$ thin films and sapphire substrate was $Li_{0.5}Ni_{0.5}O$ [$1\bar{2}1$] // sapphire [$11\bar{2}0$] and $Li_{0.5}Ni_{0.5}O$ [111] // sapphire [0001]. The cube-on-hexagonal epitaxial relationship was the same as that reported previously for similar samples (Sakata *et al.*, 2004; Yang *et al.*, 2014). The φ scan around the nonspecular NiO ($1\bar{1}1$) Bragg positions showed sixfold symmetry (not shown here). This is because two types of terraces formed alternately on the sapphire (0001) face, with 0.2 nm-high steps (Yamauchi *et al.*, 2012). We also recorded the X-ray intensities of six $1\bar{1}1$ and $2\bar{2}2$ diffraction peaks.

5.2. Debye temperature of an $Li_{0.5}Ni_{0.5}O$ epitaxial thin film

Fig. 2 shows one of the six X-ray rocking curves around the $1\bar{1}1$ Bragg peaks of the NiO and $Li_{0.5}Ni_{0.5}O$ thin films. The average full width at half-maximum of the $Li_{0.5}Ni_{0.5}O$ thin film (5.48°) was much larger than that of the NiO thin film (1.60°). This suggests that the crystal quality was lowered after Li doping.

The average integrated intensity ratio R_1 between the $1\bar{1}1$ and $2\bar{2}2$ Bragg peaks of the $Li_{0.5}Ni_{0.5}O$ epitaxial thin film was calculated to be 2.5 (2). The contribution of thermal diffuse scattering (TDS) to the measured intensity was neglected in our analysis, because the TDS correction was small (less than 4% even in imperfect single-crystal silicon; Matsumuro *et al.*, 1990; Chipman & Batterman, 1963) in our samples compared with the statistical fluctuation, which was about 7.6% in the NiO thin film. If we assume that all Li atoms are substituted at
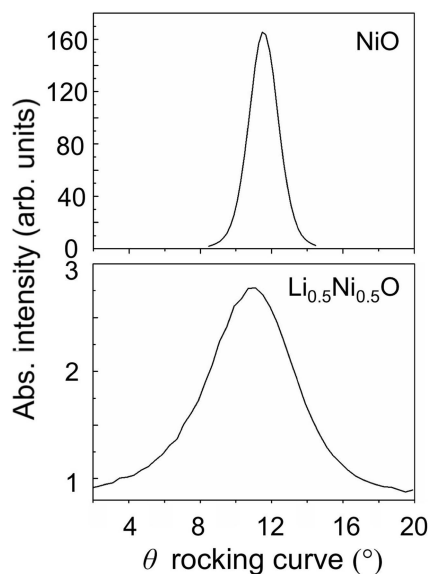

Figure 2
X-ray rocking curves around the $1\bar{1}1$ Bragg peaks of NiO and $Li_{0.5}Ni_{0.5}O$ thin films.

Table 1
B_1 and B_{NiO} factors, Debye temperature θ_M, r.m.s. amplitude of atomic vibration $\overline{u^2}^{1/2}$, ($1\bar{1}1$) lattice spacing $d_{1\bar{1}1}$, and ratio $r = \overline{u^2}^{1/2}/d_{1\bar{1}1}$ of $Li_{0.5}Ni_{0.5}O$ and NiO thin films at 298 K.

Sample	B_1 or B_{NiO} (Å²)	θ_M (K)	$\overline{u^2}^{1/2}$ (Å)	$d_{1\bar{1}1}$ (Å)	r (%)
$Li_{0.5}Ni_{0.5}O$	1.8 (4)	281 (39)	0.15 (2)	2.368 (4)	6.3 (8)
NiO	0.939	317.4 (Freer, 1981)	0.11	2.395 (2)	4.6

Ni atom positions, the composition of the $Li_{0.5}Ni_{0.5}O$ epitaxial thin film is uniform and structural disorder is neglected, the diffracted intensity from the $Li_{0.5}Ni_{0.5}O$ epitaxial film is

$$I(hkl)^{obs}_{Li_{0.5}Ni_{0.5}O} \propto |F(hkl)^{cal}_{Li_{0.5}Ni_{0.5}O}|^2 \, L_p^{hkl}$$
$$\times t^2_{Li_{0.5}Ni_{0.5}O} \exp[-2B(\sin\theta_{hkl}/\lambda)^2]. \quad (4)$$

Let us introduce the ratio S_1^{cal} of the square of the calculated structure factors:

$$S_1^{cal} \equiv \frac{|F(1\bar{1}1)^{cal}_{Li_{0.5}Ni_{0.5}O}|^2}{|F(2\bar{2}2)^{cal}_{Li_{0.5}Ni_{0.5}O}|^2}. \quad (5)$$

The values of S_1^{cal} are estimated to be 0.331 and 0.328 when we assume that the NiO and $Li_{0.5}Ni_{0.5}O$ films have the NaCl crystal structure and use the atomic scattering factors (Brown *et al.*, 2006) for their neutral atoms (Li, Ni and O) and ions (Li^+, Ni^{2+} and O^{2-}), respectively. The calculated results were almost the same. Let us define the observed integrated intensity ratio R_1:

$$R_1 \equiv \frac{I(1\bar{1}1)^{obs}_{Li_{0.5}Ni_{0.5}O}}{I(2\bar{2}2)^{obs}_{Li_{0.5}Ni_{0.5}O}}. \quad (6)$$

The averaged value of R_1 for the six equivalent reflections was 2.5 (2). Substituting equation (4) into equation (6) allows us to derive the formula for B_1 as follows:

$$B_1 = -0.5\ln(R_1 L_p^{2\bar{2}2}/S_1^{cal} L_p^{1\bar{1}1})$$
$$/[(\sin\theta_{1\bar{1}1}/\lambda)^2 - (\sin\theta_{2\bar{2}2}/\lambda)^2]. \quad (7)$$

The B_1 factor of $Li_{0.5}Ni_{0.5}O$ was calculated to be 1.8 (4) Å² when we used parameters observed from the $Li_{0.5}Ni_{0.5}O$ films: $\theta_{1\bar{1}1} = 12.19°$ and $\theta_{2\bar{2}2} = 24.88°$, and ($1\bar{1}1$) lattice spacing = 2.368 (4) Å. The corresponding Debye temperature was 281 (39) K according to equations (1) and (2). The error originates from that of B_1, and it is a little larger than that already determined by X-ray diffraction (Herbstein, 1961), so it may be caused by the large statistical fluctuation of integrated intensity. The corresponding r.m.s. amplitude of atomic vibration was evaluated to be 0.15 Å, as shown in Table 1. The ratio r between the r.m.s. amplitude of atomic vibration and the ($1\bar{1}1$) lattice spacing of the $Li_{0.5}Ni_{0.5}O$ thin film was 6.3%. This value is larger than that of ideal bulk NiO (4.6%; Freer, 1981), which suggests that Li doping increased the lattice thermal vibration (Borca *et al.*, 2000). D_1 is written as $\exp[-2B_1(\sin\theta_{1-11}/\lambda)^2]$ and is here called the real Debye–Waller factor for the $Li_{0.5}Ni_{0.5}O$ thin film.

5.3. Estimation of the effect of atomic disorder caused by Li doping on the X-ray diffraction intensity

In order to obtain the structure parameter that can be used to estimate the effect of atomic disorder [$\exp(\delta)$] caused by Li doping on the X-ray diffraction intensity of an $Li_{0.5}Ni_{0.5}O$ thin film, let us propose a factor D_2 from the X-ray $1\bar{1}1$ intensity ratio between $Li_{0.5}Ni_{0.5}O$ and NiO as shown in Fig. 1. If we assume that all of the Li atoms are substituted for Ni atoms and the composition of the $Li_{0.5}Ni_{0.5}O$ epitaxial thin film is uniform (Fig. 3a), then structural disorder can be neglected.

Let us define the measured average intensity ratio R_2 between the $1\bar{1}1$ Bragg peaks of the $Li_{0.5}Ni_{0.5}O$ and NiO films:

$$R_2 \equiv \frac{I(1\bar{1}1)^{obs}_{Li_{0.5}Ni_{0.5}O}}{I(1\bar{1}1)^{obs}_{NiO}}. \qquad (8)$$

The average value of R_2 for the six equivalent reflections was 0.029 (4). We also define

$$S_2^{cal} \equiv \frac{|F(1\bar{1}1)^{cal}_{Li_{0.5}Ni_{0.5}O}|^2}{|F(1\bar{1}1)^{cal}_{NiO}|^2}. \qquad (9)$$

The value of S_2^{cal} is 0.148 when we assume that the NiO and $Li_{0.5}Ni_{0.5}O$ films have the NaCl crystal structure and use the atomic scattering factors for their neutral atoms. The formula for our proposed parameter B_2 is obtained after we substitute equation (4) into equation (8):

$$B_2 = -0.5[\ln(R_2 L_p^{NiO1\bar{1}1} t_{NiO}^2 / S_2^{cal} L_p^{1\bar{1}1} t_{Li_{0.5}Ni_{0.5}O}^2) \\ - 2B_{NiO}(\sin\theta_{1\bar{1}1}^{NiO}/\lambda)^2]/(\sin\theta_{1\bar{1}1}/\lambda)^2. \qquad (10)$$

B_2 was evaluated to be 6.5 (15) Å^2 using the B_{NiO} value of 0.939 Å^2 obtained from θ_M (317.4 K at RT; Freer, 1981) of NiO according to equations (1) and (2). We also used parameters ($\theta_{1\bar{1}1}^{NiO} = 12.05°$) observed from the NiO film. These obtained parameters, the r.m.s. amplitude of atomic vibration and its ratio compared with the lattice spacing are listed in Table 2. D_2 is written as $\exp[-2B_2(\sin\theta_{1\bar{1}1}/\lambda)^2]$ and is here called the pseudo-Debye–Waller factor for the $Li_{0.5}Ni_{0.5}O$ thin film. B_2 is much greater than B_1. We do not consider the atomic disorder when obtaining the B_1 value. To consider the difference between B_1 and B_2, let us assume the relation of D_2 and D_1 using the atomic disorder parameter expressed as $D_2 = \exp(\delta)D_1$. $\exp(\delta)$ was evaluated to be 0.66 using NiO as
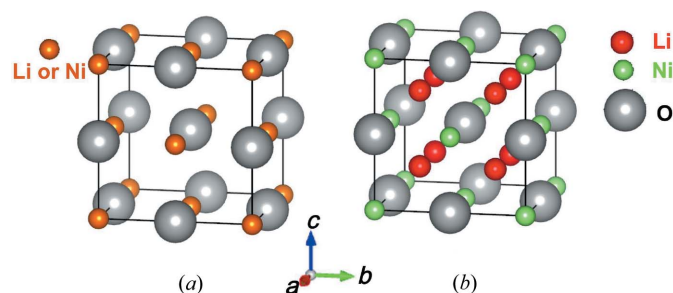

Figure 3
Crystal structure models of $Li_{0.5}Ni_{0.5}O$ with (a) all of the Li atoms substituted for Ni atoms and (b) all of the Li atoms located in interstitial sites.

Table 2
B_2 and B_3 factors, Debye temperature θ_M, r.m.s. amplitude of atomic vibration ($\overline{u^2}^{1/2}$), ($1\bar{1}1$) lattice spacing $d_{1\bar{1}1}$, and ratio $r = \overline{u^2}^{1/2}/d_{1\bar{1}1}$ of $Li_{0.5}Ni_{0.5}O$ thin films at 298 K.

Site	B_2 or B_3 (Å^2)	θ_M (K)	$\overline{u^2}^{1/2}$ (Å)	$d_{1\bar{1}1}$ (Å)	r (%)
Substitutional	6.5 (15)	147 (22)	0.29 (3)	2.368 (4)	12.2 (13)
Interstitial	3.1 (15)	213 (45)	0.20 (6)	2.368 (4)	8.4 (25)

reference. This value is much smaller than unity, which suggests that the range in which the atoms are located might be ca 0.14 Å wider than that for B_1. In general, Debye–Waller factors may include not only the influence of the thermal disorder but also that of the atomic disorder. The structural disorder that we evaluated looks to have a very small influence on B_1. Furthermore, let us assume another extreme case where all of the Li atoms are located on interstitial sites. Interstitial Li atoms are found not only in cubic Li-doped NiO (Guo et al., 2013) but also in many other crystal structures like ZnO (Chawla et al., 2009), ZnSe (Sasaki et al., 1993) and Li_3NbO_4 (McLaren et al., 2004). The positions of the Li atoms are (1/4, 1/4, 1/4), (3/4, 1/4, 1/4), (3/4, 3/4, 1/4), (1/4, 3/4, 1/4), (1/4, 1/4, 1/2), (3/4, 1/4, 1/2), (3/4, 3/4, 1/2), (1/4, 3/4, 1/2), as shown in Fig. 3(b). Therefore, the structure factor of $Li_{0.5}Ni_{0.5}O$ along [$1\bar{1}1$] changes to

$$|F(1\bar{1}1)^{cal}_{Li_{0.5}Ni_{0.5}O}|^2 = 16[0.5f(1\bar{1}1)_{Ni} - f(1\bar{1}1)_O]^2. \qquad (11)$$

Let us introduce B_3 for all the Li atoms sitting in interstitial sites. The value is 3.1 (15) Å^2 using equations (8) and (11), as shown in Table 2. The difference between B_3 for the Li interstitial model and B_1 is smaller than that between B_2 for the Li substitute model and B_1. This implies that some Li atoms are probably located in the interstitial sites in a heavily doped $Li_{0.5}Ni_{0.5}O$ thin film. These results help us to understand the physical properties of $Li_xNi_{1-x}O$ to develop $Li_xNi_{1-x}O$-based devices.

6. Concluding remarks

In conclusion, the conventional B_1 factor of an $Li_{0.5}Ni_{0.5}O$ thin film was estimated to be 1.8 (4) Å^2 using X-ray diffraction by considering the $1\bar{1}1$ and $2\bar{2}2$ reflections. The corresponding Debye temperature was 281 (39) K. Furthermore, the pseudo-Debye–Waller factor of the $Li_{0.5}Ni_{0.5}O$ thin film was obtained using the intensity ratio between the $1\bar{1}1$ Bragg peaks of $Li_{0.5}Ni_{0.5}O$ and NiO thin films. The atomic disorder parameter that we proposed was evaluated to be 0.66. The disorder may include combined effects of thermal vibration, interstitial atoms and defects caused by Li doping. Interstitial Li atoms could be present in heavily Li-doped $Li_{0.5}Ni_{0.5}O$ thin films because the proposed B_3 factor was smaller than B_2 determined for a film with Li ions only in Ni sites.

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