分子研研究会「放射光の現状と将来計画」
2002年11月13日～14日（岡崎）

放射光を用いたミリ波分光の現状と将来

神戸大学分子フォトサイエンス研究センター

太田　仁

共同研究者

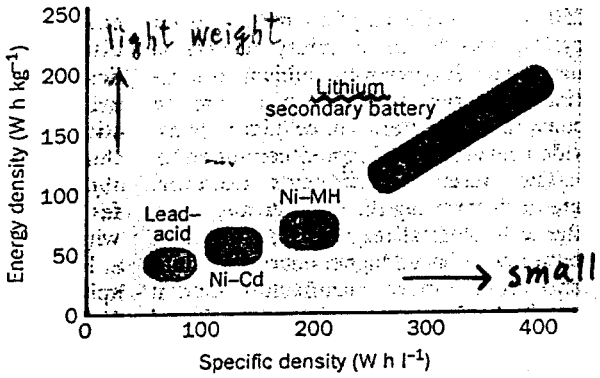
神戸大学　池内洋仁
小野俊介
上田敬史
川上幹児
長坂雄太
平野智也

難波孝夫

三重大学　平野敦
東京工業大学　菅野了次

$LiNiO_2$ has two interesting aspects

1) 2D triangular lattice antiferromagnet
2) superionic conductor
   promising for a positive electrode material in secondary Li batteries



Gravimetric versus volumetric energy density for various battery types. Derived from ref. 10.

$LiCoO_2$ is already in use as a battery

$LiNiO_2$ next generation?

$Li_{1-x}Ni_{1+x}O_2$ Goodenough *et al.*, J. Phys. Chem. Solids **5** (1958) 107.
x depends on the sintering condition strongly

x=0 sample shows best performance as a battery

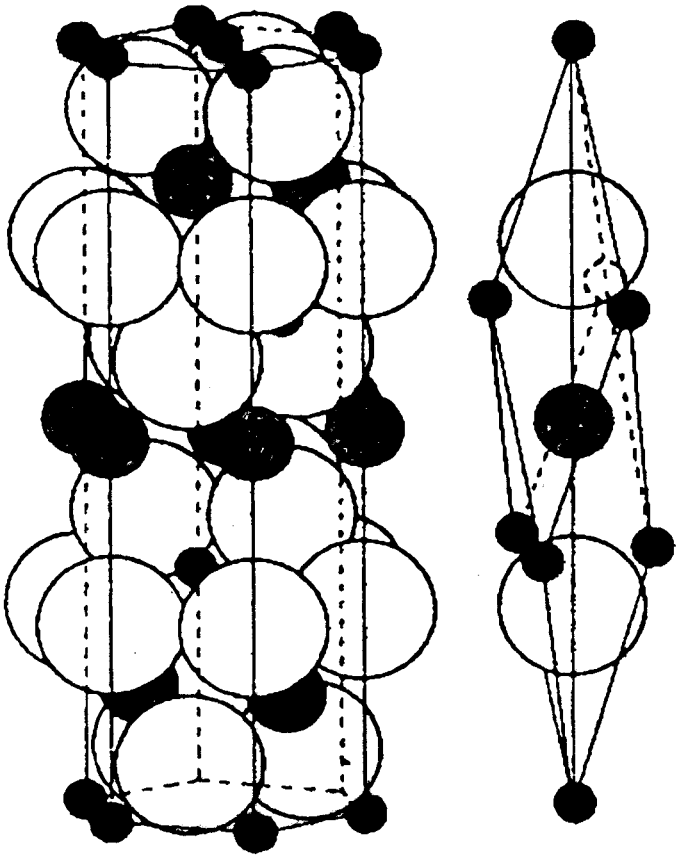
Kanno *et al.* developed a method to control x

$Li_{0.996}Ni_{1.004}O_2$ sintered at 650°C in O_2
$Li_{0.946}Ni_{1.054}O_2$ sintered at 850°C in O_2

R. Kanno *et al.*, J. Solid State Chem. **110** (1994)

$LiMn_2O_4$

Crystal structure and Physical properties of $LiNiO_2$



:Oxygen :Lithium :Nickel

2-D layered rock-salt structure

- **Triangular lattice antiferromagnets**
- **Super ionic conductor**

In our previous **submillimeter wave ESR** measurements of **$LiNiO_2$**, we observed the decrease of transmission above **204K** .

H. Ohta *et al.*:Physica B **237** (1997) 64.

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The origin of this phenomenon ?

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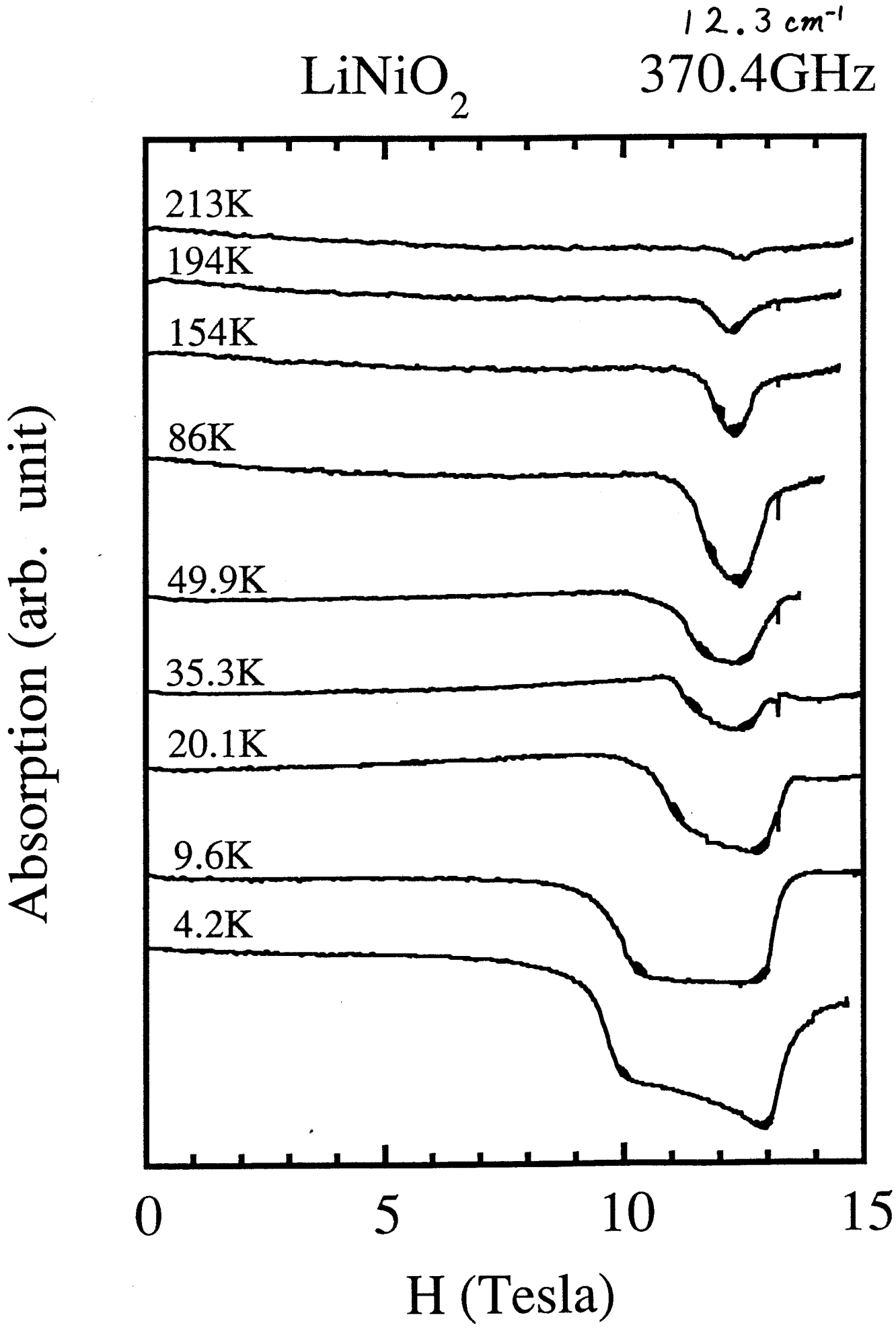
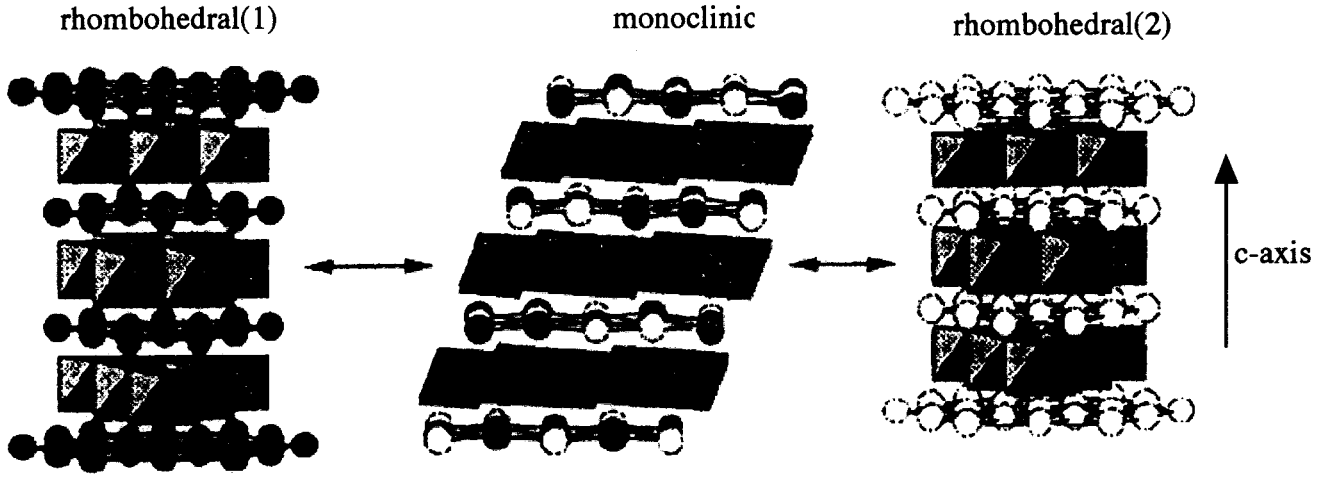
Millimeter wave spectroscopy

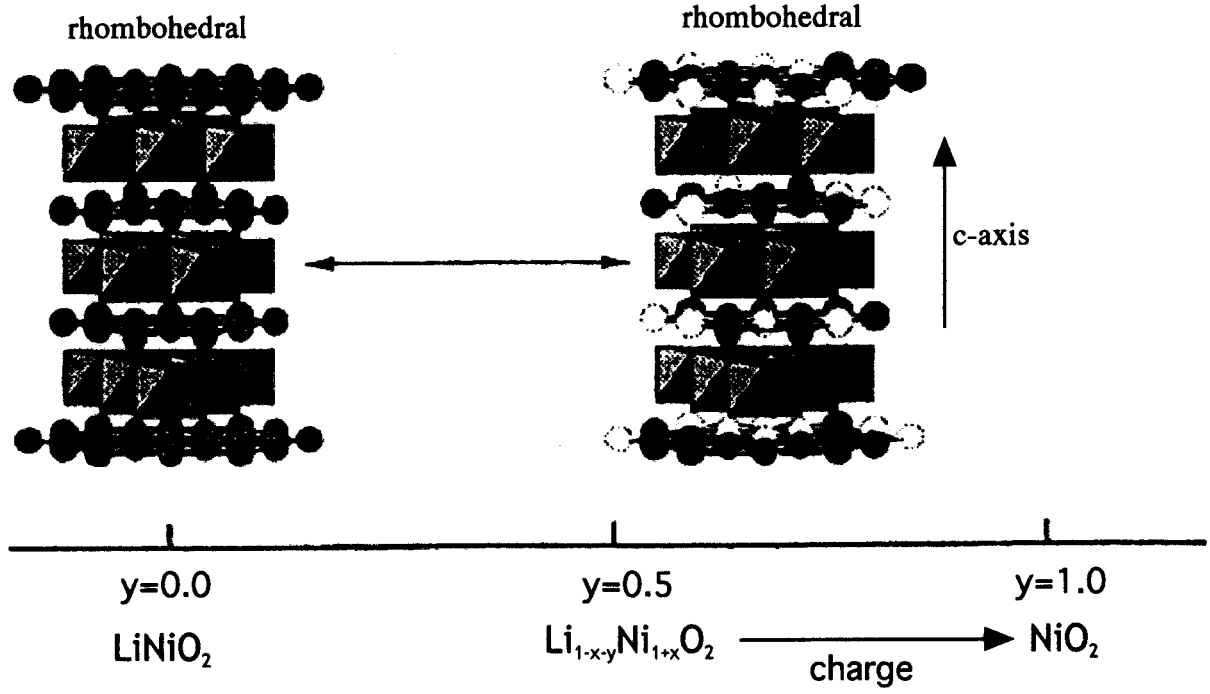

12.3 cm-1
LiNiO2
370.4GHz
213K
194K
154K
86K
49.9K
35.3K
20.1K
9.6K
4.2K
Absorption (arb. unit)
0
5
10
15
H (Tesla)

The charge-discharge structure of $LiNiO_2$

stoichiometry



non-stoichiometry



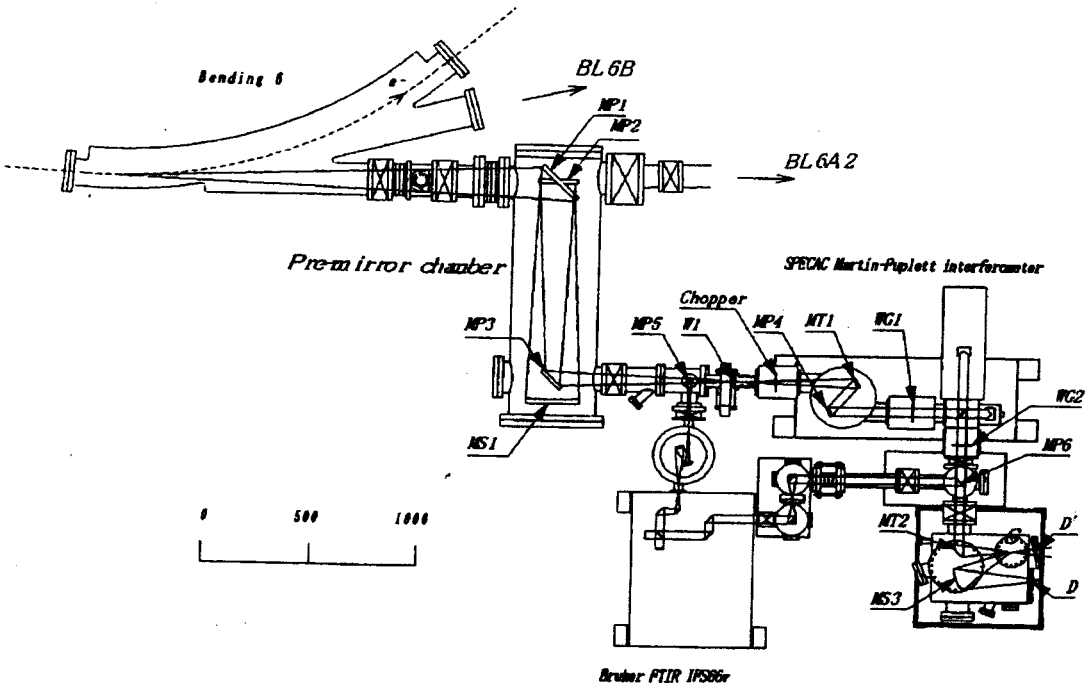
$LiNiO_2$ ⟶ $Li_{1-x}Ni_{1+x}O_2$

stoichiomerty non-stoichiometry

the electrical charge and discharge characteristics was degraded as the x in $Li_{1-x}Ni_{1+x}O_2$ is increased because Ni ions, which entered the Li sites, prevent the diffusion of Li ions .

Experimental

Beam line BL6A1 of UVSOR
(Institute of Molecular Science in Okazaki)



T. Nanba: Rev. Sci. Instrum. **60** (1989) 1680

Beam source: synchrotron radiation
Interferometer: Martin Puplett type Fourier transform spectrometer
Detector: InSb and Ge bolometer
Spectral range: 6-60 cm^{-1} (low-pass filter<22 cm^{-1})
30-150 cm-1
Temperature: 79-380 K

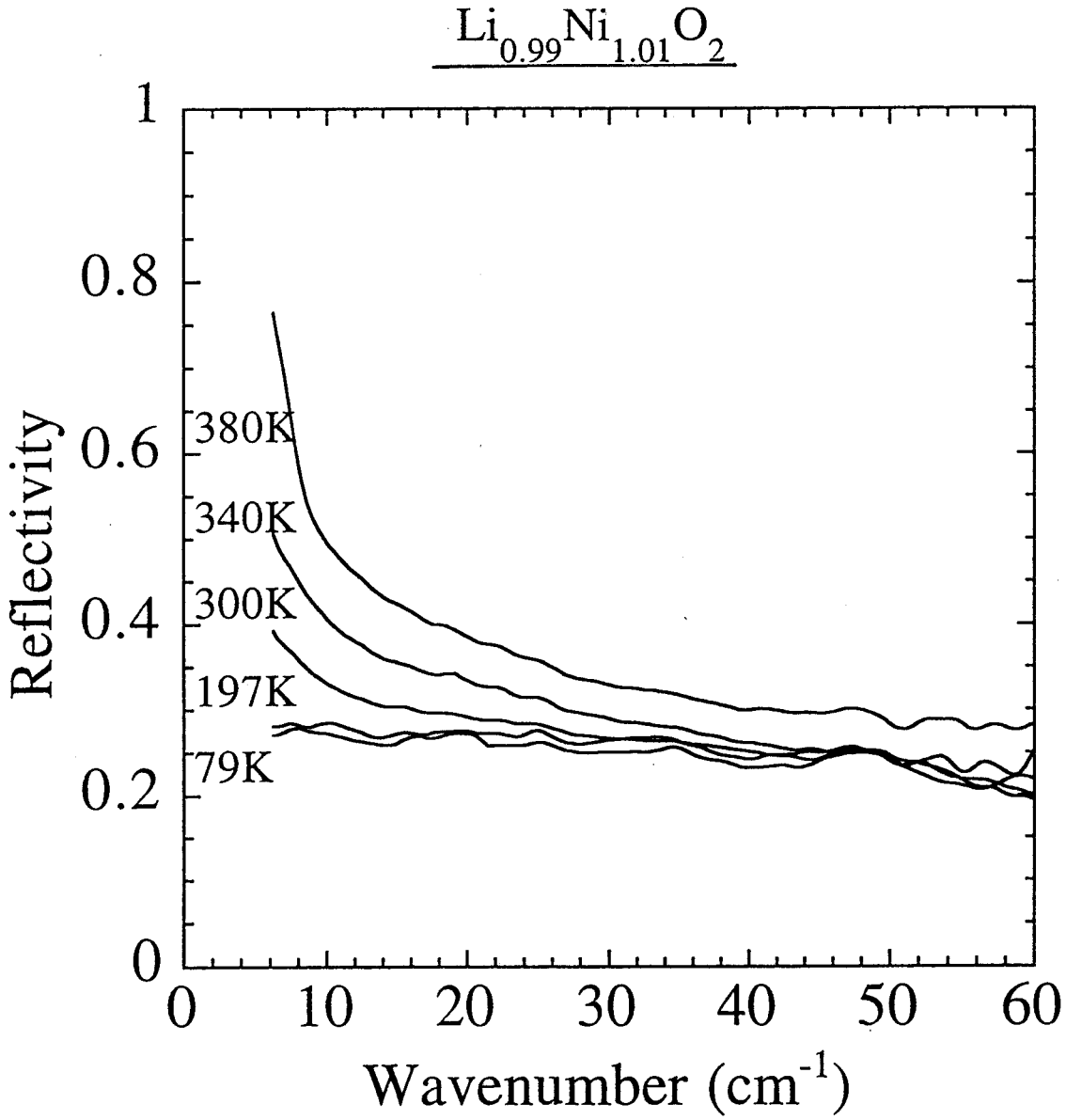
Sample (powder pellets)

$Li_{1-x}Ni_{1+x}O_2$ (x=0.01, 0.05, 0.11) $Li_{1-x}NiO_2$

$LiCoO_2$ $Li_{1-x}CoO_2$

$LiMn_2O_4$

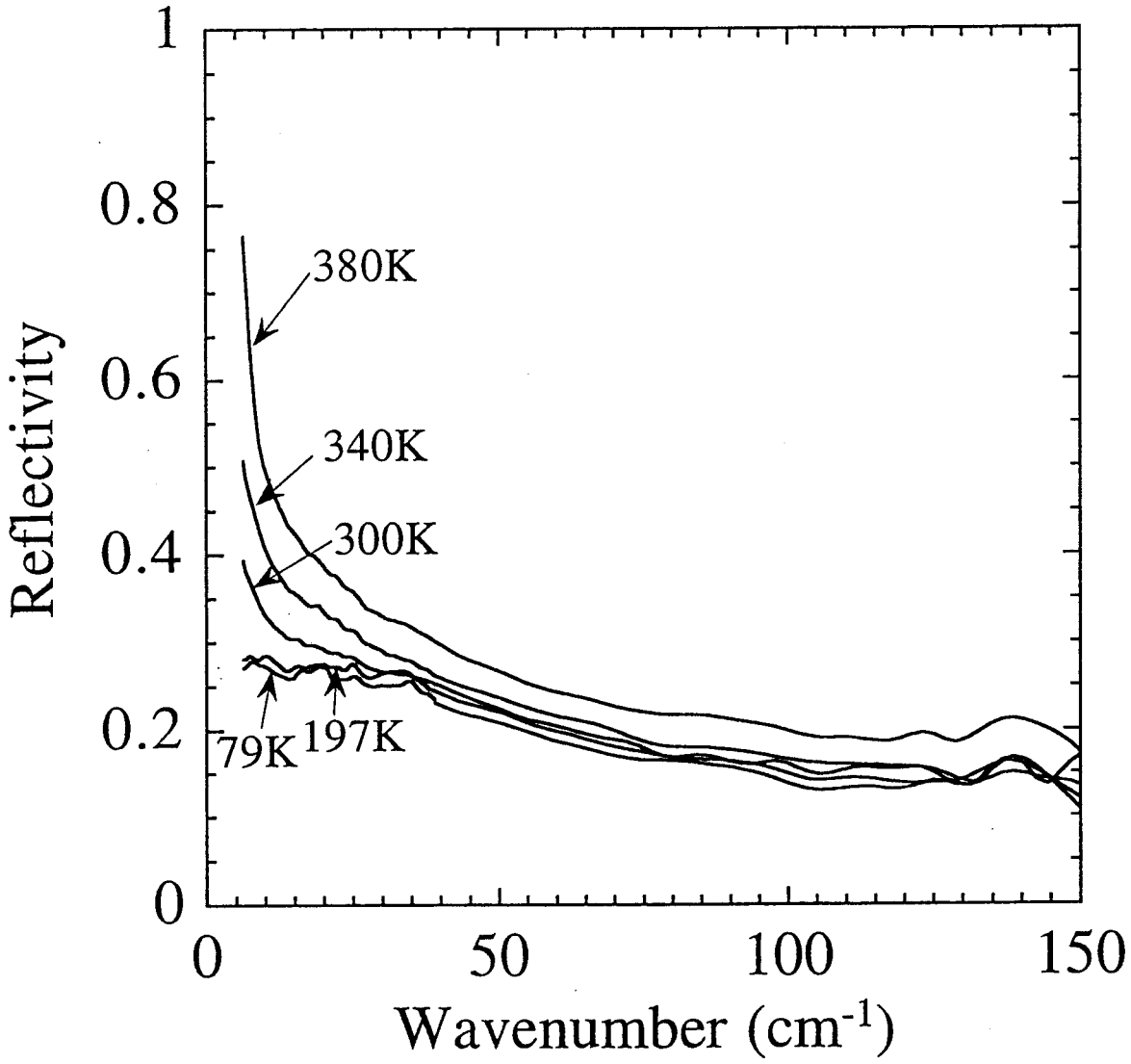
Reference: Au mirror



- The rise of the reflectivity in the low energy region above 300 K.

Observed for the first time!

$Li_{0.99}Ni_{1.01}O_2$



What is the origin of the rise of the reflectivity?

1. Magnetic origin
2. Phonon excitation
3. The motion of Li^+ ions in $LiNiO_2$

1) Analogies between $LiCoO_2$ and $LiNiO_2$

<Lattice parameters and symmetry>

	structure	a (Å)	c (Å)
$LiNiO_2$	layered rock-salt	2.875	14.18
$LiCoO_2$	layered rock-salt	2.82	14.08

↓

$LiNiO_2$ has almost **the same crystal structure** as those of **$LiCoO_2$**

same vibrational phonon modes are expected

2) IR and Raman studies of $LiCoO_2$

$R\bar{3}m$ $\quad \Gamma_{vib} = A_{1g}(R)+E_g(R)+2A_{2u}(IR)+2E_u(IR)$

IR: 271, 537, 595, 653 (cm^{-1}) ***Raman***:486, 595 (cm^{-1})

↓

The phonon modes are in the spectral region,

$271 < \omega < 653$ **(cm^{-1})**

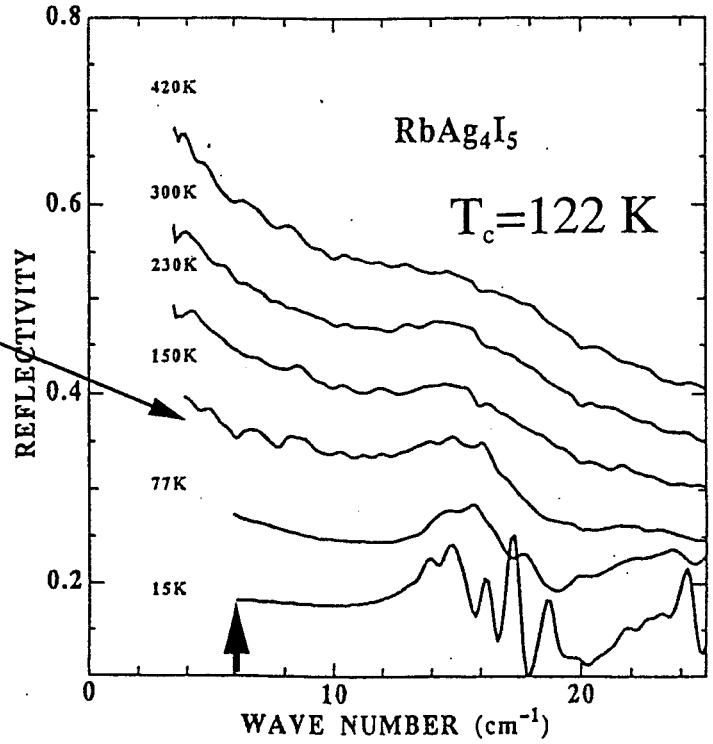
W. Huang *et al* .:Solid State Ionics. 86 (1996) 395.

No contribution of the phonon
in the spectral region **5 ~ 60** (cm^{-1}) for **$LiNiO_2$**.

Example

Reflection measurements in millimeter wave region of **alkali silver iodide super ionic conductor MAg_4I_5 (M=Rb,K, and NH_4)**

Ions start to move above T_c



Awano *et al* .:Solid State Ion. **53** (1992) 1269

They obsereved the **increase of the reflectivity** of these substances above T_c.

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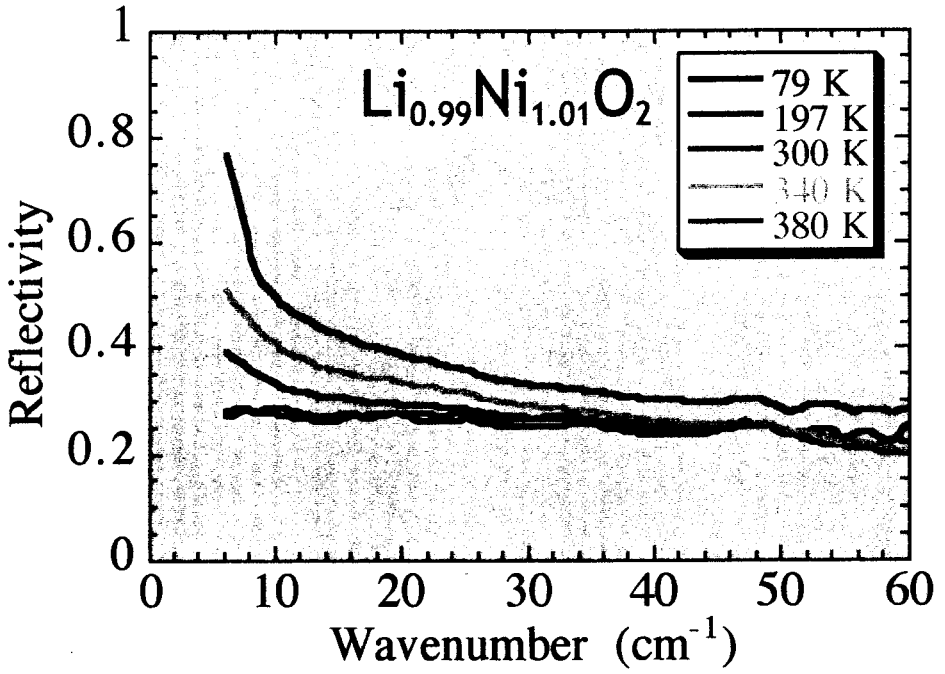
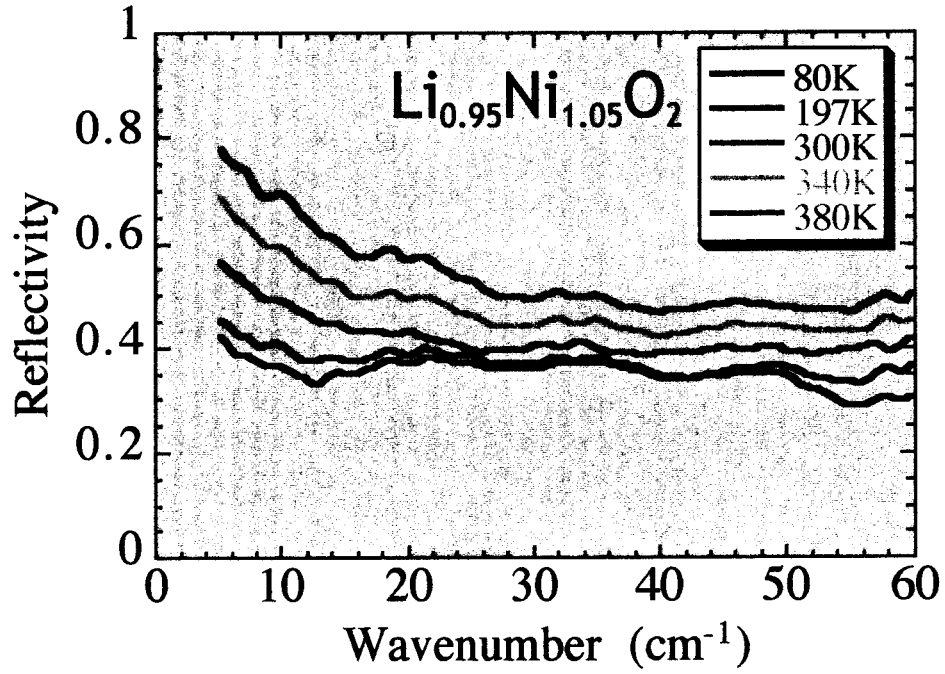
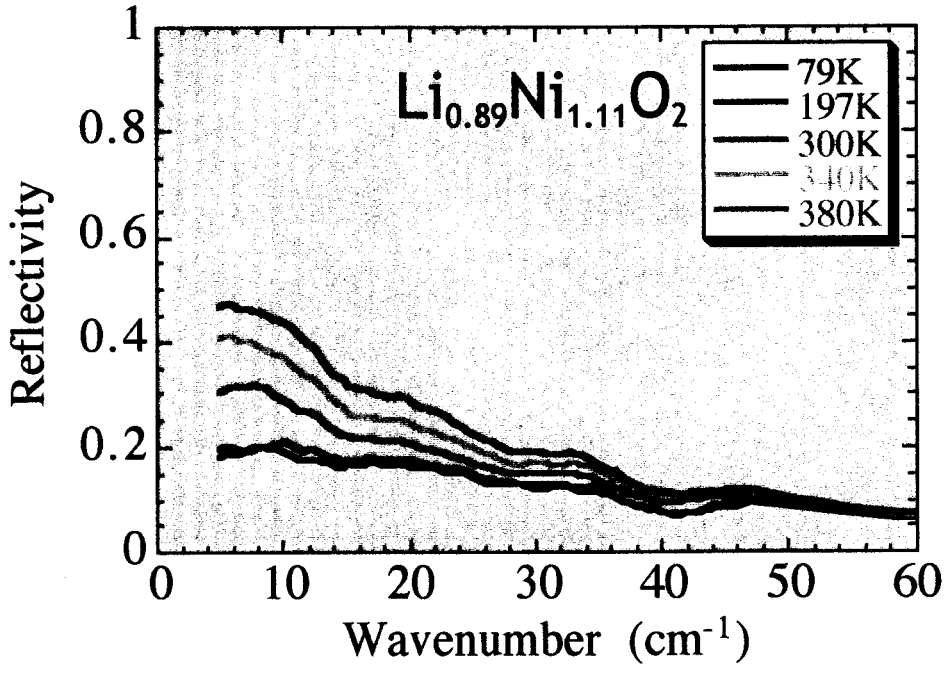
Effect of the diffusive motion of Ag ion


$Li_{0.99}Ni_{1.01}O_2$
79 K
197 K
300 K
340 K
380 K
Reflectivity
Wavenumber (cm^{-1})


$Li_{0.95}Ni_{1.05}O_2$
80K
197K
300K
340K
380K
Reflectivity
Wavenumber (cm^{-1})


$Li_{0.89}Ni_{1.11}O_2$
79K
197K
300K
340K
380K
Reflectivity
Wavenumber (cm^{-1})

Discussion

We assume that Li^+ ions move like electrons in metals because $LiNiO_2$ is a superionic conductor.

the origin of the rise of the reflectivity above 300 K

↓

a plasma reflection below the plasma frequency ω_p.

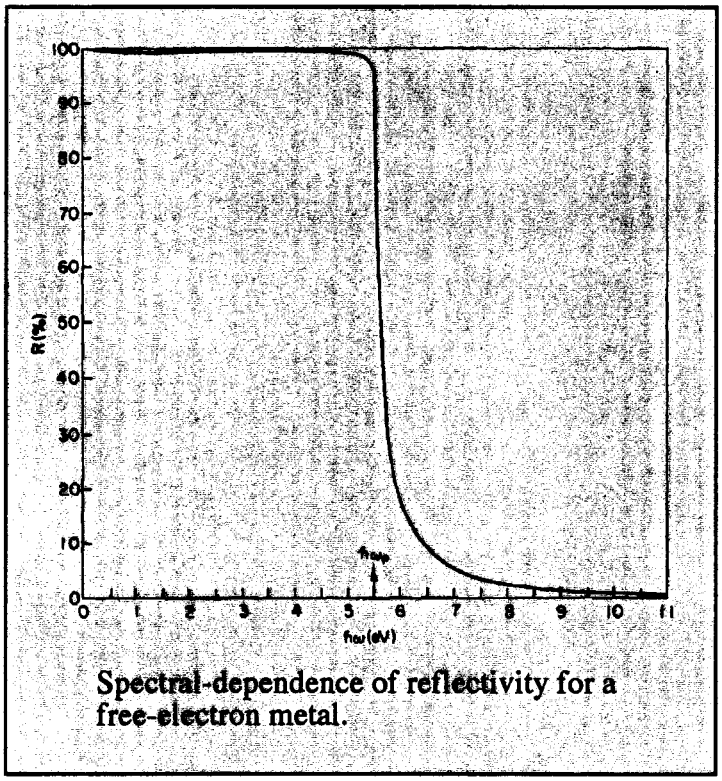
$$\omega_p = \sqrt{\frac{Ne^2}{\varepsilon m^*}}$$

N : the number of mobile ions
m : the effective mass of the ion
ε : the dielectric constant

Assuming $N \approx 10^{19}\ cm^{-3}$ ⟶ the order of $\omega_p \approx 10\ cm^{-1}$

Drude model

The reflectivity R can be written as $R = \dfrac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$



Spectral-dependence of reflectivity for a free-electron metal.

$$k = \left\{\frac{1}{2}\left[\varepsilon_1^2 + \varepsilon_2^2\right]^{\frac{1}{2}} - \varepsilon_1\right\}^{\frac{1}{2}} \qquad \varepsilon_1 = 1 - \frac{\omega^2\tau^2}{(1+\omega^2\tau^2)}$$

$$n = \left\{\frac{1}{2}\left[\varepsilon_1^2 + \varepsilon_2^2\right]^{\frac{1}{2}} + \varepsilon_1\right\}^{\frac{1}{2}} \qquad \varepsilon_2 = \frac{\omega_p^2\tau}{\omega(1+\omega^2\tau^2)}$$

τ : mean free time

The slope of the increase of the reflectivity can be interpreted by τ. The increase of τ contributes to the steep increase of the reflectivity.

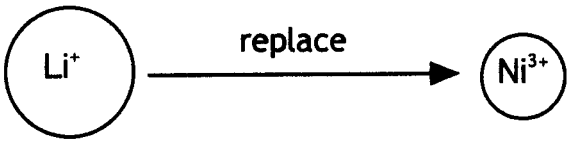
Therefore, the gentle increase of the reflectivity in x=0.05 sample compared to x=0.01 sample can be interpreted by the shorter mean free time in x=0.05 than that in x=0.01.

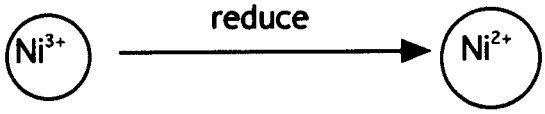
We assume that the difference of mean free time is caused by the lattice distortion.

Difference of ionic radii

Ni^{3+} : 0.60Å
Ni^{2+} : 0.70Å
Li^{+} : 0.72Å at octahedral sites

As the x increases, the cation disordering occur.

Li^{+} site 

Ni^{3+} site 

This causes a lattice distortion, and the decrease of τ.

↓

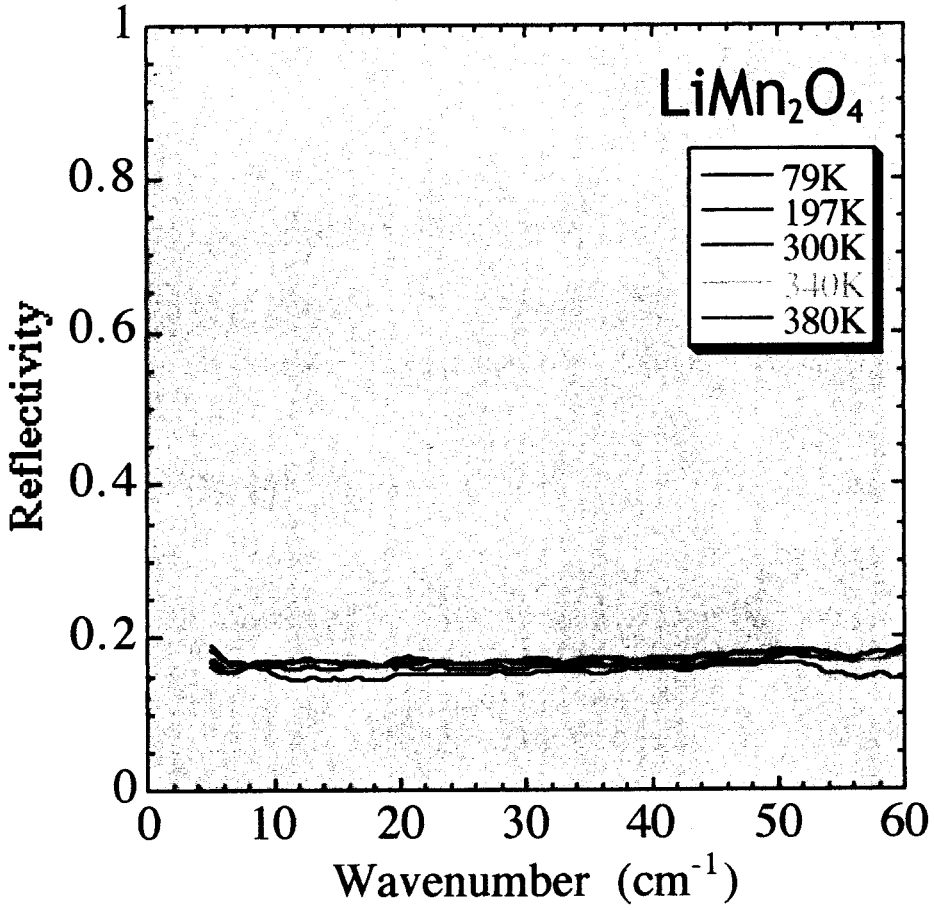
mean free time τ : x=0.01 > x=0.05
battery performance : x=0.01 > x=0.05

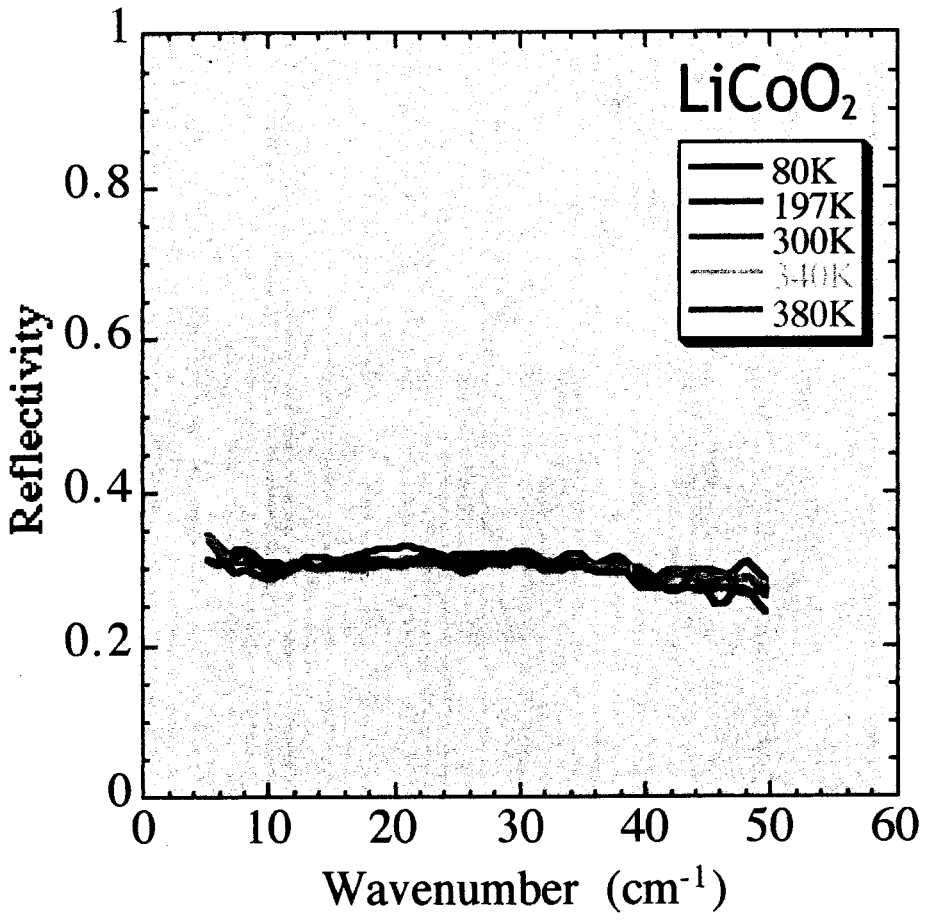
On the other hand,

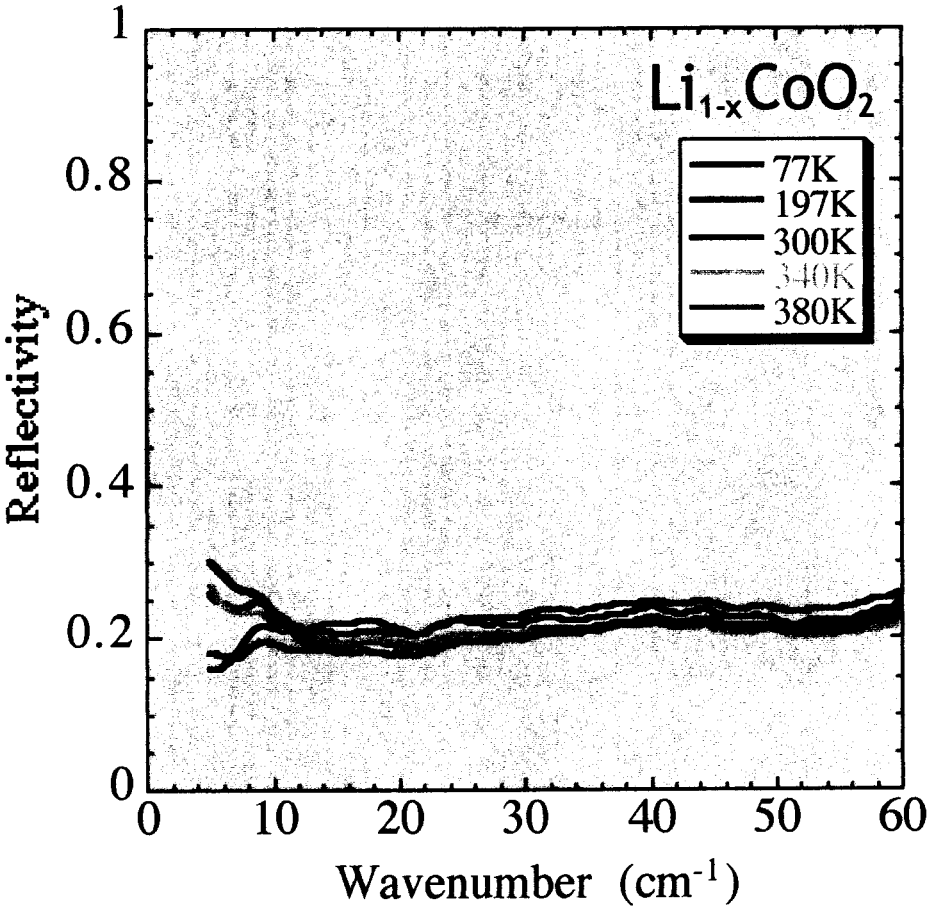
we can no longer explain the reflectivity of x=0.11 in the same way.

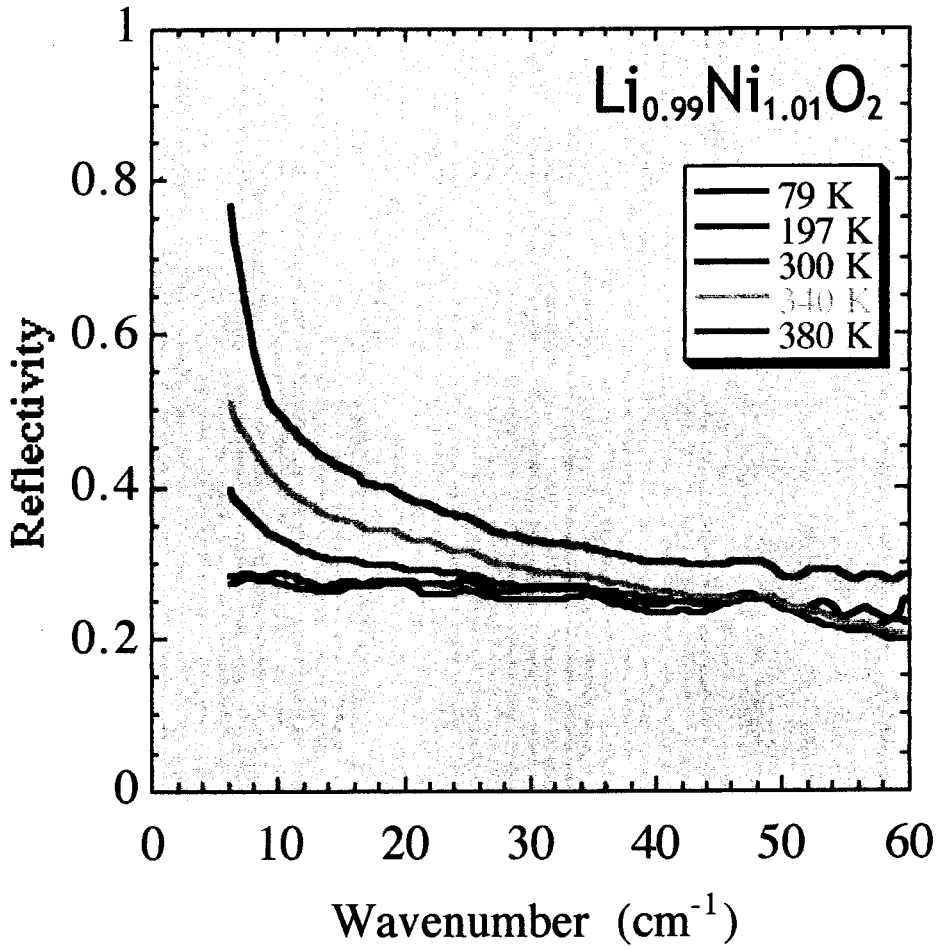
The excessive Ni ions seem to break the electrical conduction of Li ions.

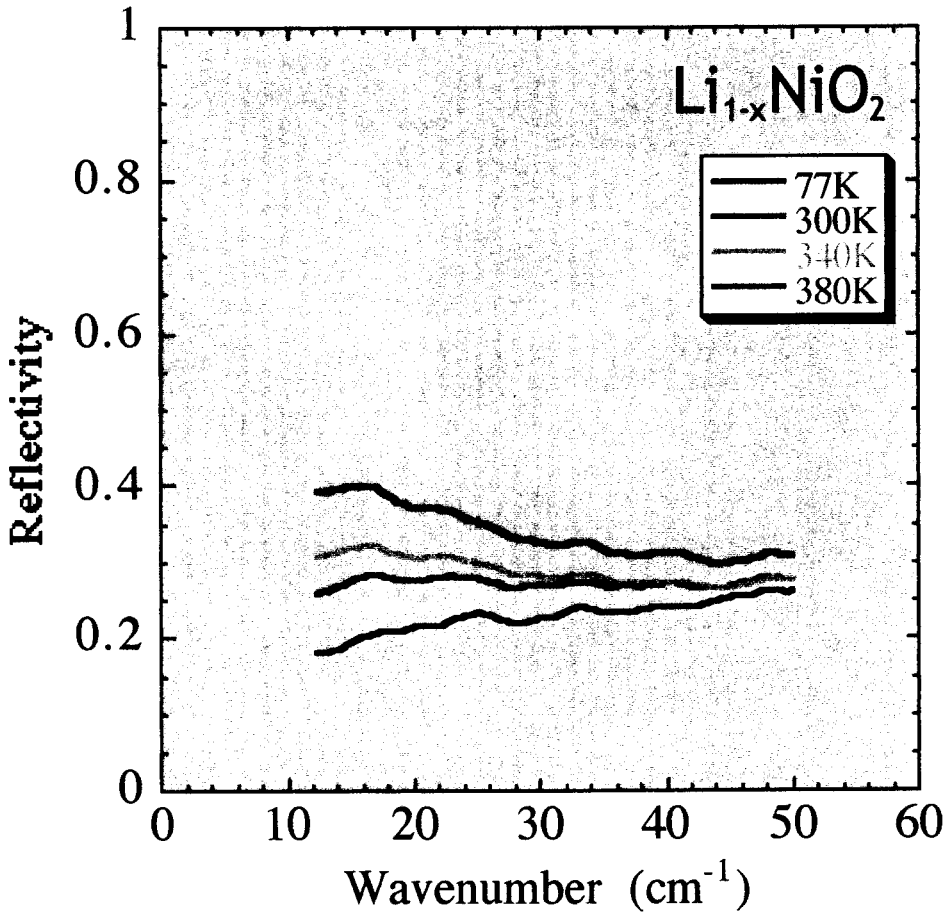
The dominant conduction mechanism may change to a hopping conduction between x=0.05 and x=0.11?

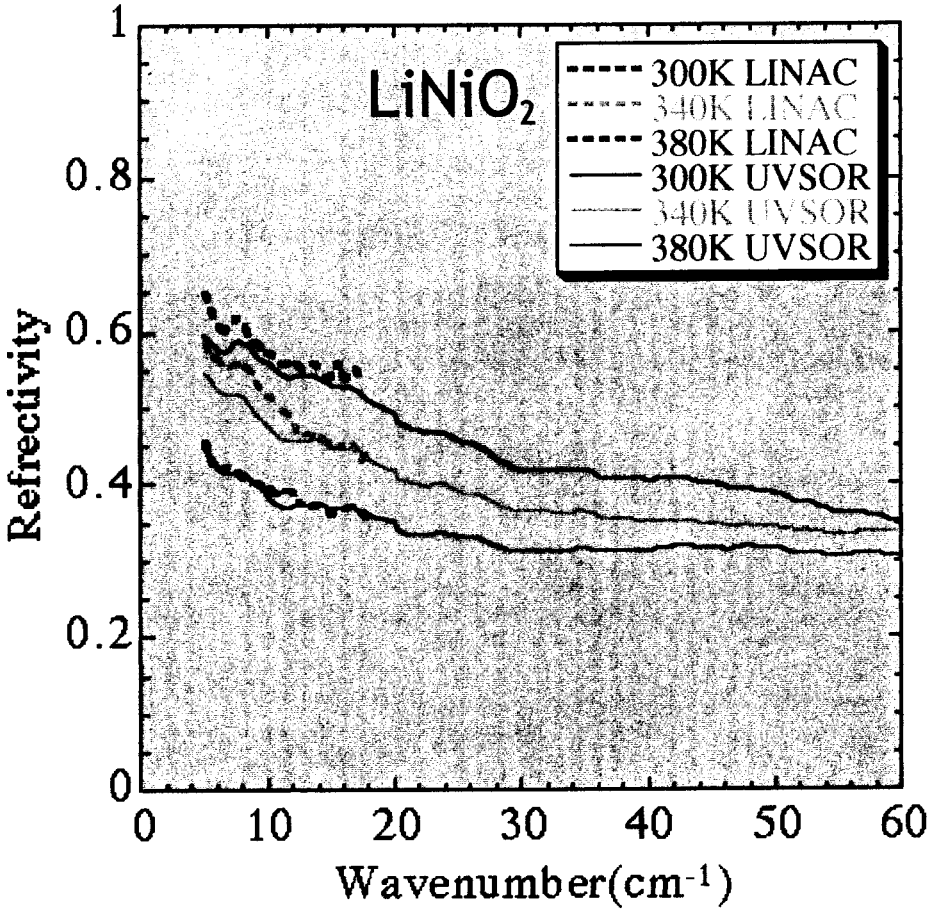

LiMn2O4
79K
197K
300K
340K
380K
Reflectivity
Wavenumber (cm-1)
0
0.2
0.4
0.6
0.8
1
0
10
20
30
40
50
60


LiCoO2
80K
197K
300K
340K
380K
Reflectivity
Wavenumber (cm-1)
0
0.2
0.4
0.6
0.8
1
0
10
20
30
40
50
60


Li1-xCoO2
77K
197K
300K
340K
380K
Reflectivity
Wavenumber (cm-1)
0
0.2
0.4
0.6
0.8
1
0
10
20
30
40
50
60


$Li_{0.99}Ni_{1.01}O_2$
79 K
197 K
300 K
340 K
380 K
Reflectivity
Wavenumber (cm^{-1})
0
0.2
0.4
0.6
0.8
1
0
10
20
30
40
50
60


$Li_{1-x}NiO_2$
77K
300K
340K
380K
Reflectivity
Wavenumber (cm^{-1})
0
0.2
0.4
0.6
0.8
1
0
10
20
30
40
50
60


LiNiO2
300K LINAC
340K LINAC
380K LINAC
300K UVSOR
340K UVSOR
380K UVSOR
Refrectivity
Wavenumber(cm-1)
0
0.2
0.4
0.6
0.8
1
0
10
20
30
40
50
60

Summary

1) MMW spectroscopy can be used for the study of Li ion secondary battery substances

2) We need to clarify the origin of the rise of the reflection.

3) Coherent SR can be used for the MMW spectroscopy.

Future perspective

1) Extension of spectroscopy range
UVSOR IMR + Coherent SR(Kyoto Univ.)

2) SR + pulsed magnetic field

3) Reproducibility

4) Time resolved measurement