Raman Spectra of $LiCo_{1-y}Ni_yO_2$

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Raman spectra of lithium-cobalt-nickel oxide, $LiCo_{1-y}Ni_yO_2$ ($0 \le y \le 1$), which is a promising material for the cathodes of secondary lithium batteries, were studied. By factor group analysis, Raman-active modes of $LiCoO_2$ (y = 0) were assigned as A1g + Eg, and their atomic displacements were speculated. The theoretical results were confirmed by the observed two strong Raman band of $LiCoO_2$ (y = 0). With replacing Co with Ni, the intensities of both bands decreased drastically, and the peak wavenumbers of the lower and upper bands were up- and down-shifted, respectively.

Lithium-cobalt-nickel-oxide, $LiCo_{1-y}Ni_yO_2$ ($0 \le y \le 1$), is now attracting much attention as the cathodes of rechargeable lithium batteries[1-5] because lithium ion is electrochemically extracted and inserted with high reversibility. $LiCo_{1-y}Ni_yO_2$ ($0 \le y \le 1$) crystallizes in a layered α-$NaFeO_2$-type ($R\bar{3}m$) structure in which Li and Me (Me: Co or Ni) fill alternately the octahedral sites in the oxygen cubic close packing.[1-7] The lithium-ion extraction and insertion mechanisms such as a series of phase transition during charging and discharging have been investigated so far using X-ray diffraction (XRD). However, it is difficult to obtain detailed information about lithium such as the sites occupying in the crystal structure from XRD measurements because the atomic scattering factor of lithium is much smaller than that of cobalt or nickel. Raman spectra give information regarding the vibrations of atoms (including lithium) in crystal, and are very sensitive to the symmetry of crystal structure.[8] We have previously showed that laser Raman spectroscopy is useful as a complementary tool to XRD to study the structural changes of active materials of batteries during charging and discharging.[9] However, there have been few theoretical and experimental Raman studies on $LiCo_{1-y}Ni_yO_2$. In this communication, we report the Raman spectra of $LiCo_{1-y}Ni_yO_2$ ($0 \le y \le 1$), and discuss the effects of replacing Co with Ni in $LiCoO_2$.

$LiCo_{1-y}Ni_yO_2$ ($0 \le y \le 1$) samples were prepared by a conventional solid phase reaction using $LiNO_3$ (Wako Pure Chemical), $CoCO_3$ and $NiCO_3$ (Mitsuwa Pure Chemical) as raw materials. They were mixed, and fired at 750°C for 24 h under oxygen gas flow. The formation of rhombohedral $LiCo_{1-y}Ni_yO_2$ ($0 \le y \le 1$) was confirmed by powder XRD measurements.[1-7] Raman spectra were excited by using a 514.5 nm line (50 mW) of an argon ion laser (NEC, GLG3260). The Raman spectra were recorded using a spectrometer (Jobin-Yvon, T64000) equipped with a multichannel charge coupled device (CCD) detector. For each measurement the integration time was 20 min.

Figure 1 shows the Raman spectra of the $LiCo_{1-y}Ni_yO_2$ ($0 \le y \le 1$) powder samples. Two strong Raman bands were observed at 485 and 597 cm^{-1} for $LiCoO_2$ (y = 0). The space group of $LiCoO_2$ is $R\bar{3}m$ (D^5_{3d}) with Z = 1. By factor group analysis[10,11] we obtain

$$\begin{array}{ll} \text{for 1Li:} & \Gamma_{T'} = A2u + Eu, \\ \text{for 1Co:} & \Gamma_{T'} = A2u + Eu, \\ \text{for 2O:} & \Gamma_{T'} = A1g + Eg + A2u + Eu. \end{array}$$

where $\Gamma_{T'}$'s denote the irreducible representations of the degrees of freedom for atoms. Subtracting off the three acoustic modes (A2u + Eu), the total vibrational modes are

$$\underset{R}{A1g} + \underset{R}{Eg} + \underset{IR}{2A2u} + \underset{IR}{2Eu}.$$

The A1g and Eg modes are Raman active, and the 2A2u and 2Eu modes are IR-active. Thus, $LiCoO_2$ should exhibit two Raman bands, which were in agreement with the observed Raman bands. It should be noted that the Raman-active A1g and Eg modes are not included in $\Gamma_{T'}$'s for Li and Co atoms; that is, only the oxygen atoms vibrate in these modes. Therefore the atomic displacements of the Raman-active A1g and Eg modes of $LiCoO_2$ are speculated as shown in Figure 2. In the A1g mode the two oxygen atoms vibrate in the opposite directions parallel to the c-axis of $LiCoO_2$, while they vibrate alternately in the opposite directions parallel to the Li and Co planes in the Eg mode. We have not yet determined which mode is assigned to the higher or upper frequency band because of the lack of $LiCoO_2$ single crystal.

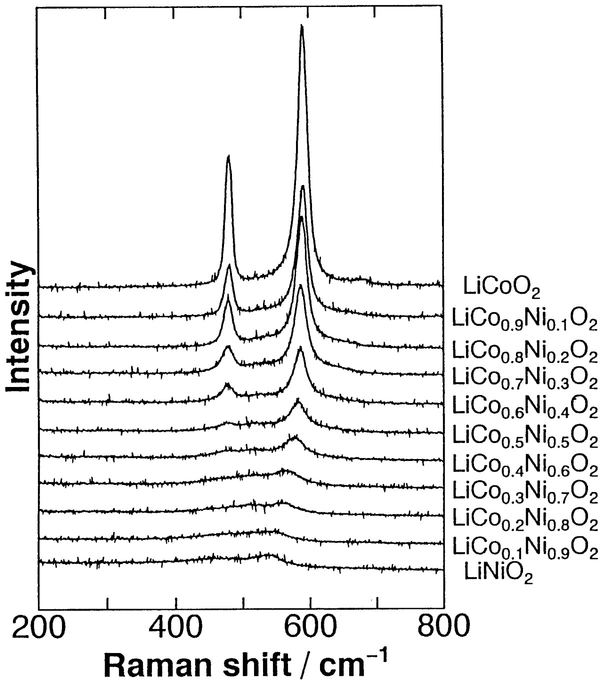

Figure 1. Raman spectra of $LiCo_{1-y}Ni_yO_2$ powder samples.

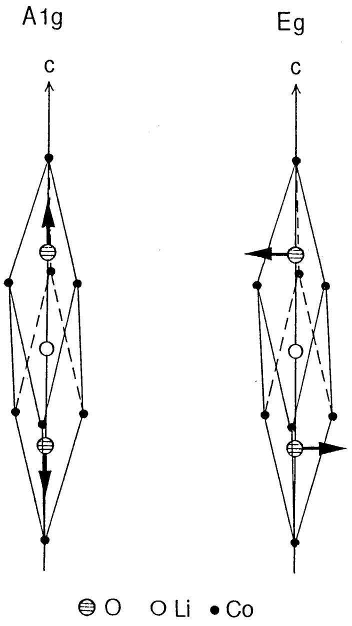

Figure 2. Atomic displacements of the Raman-active A1g and Eg modes of $LiCoO_2$.

Replacing Co with Ni does not change the space group. This was confirmed by the presence of the two Raman bands (A1g and Eg modes) of $LiCo_{1-y}Ni_yO_2$ ($0 < y \leq 1$) samples, although the intensities of both bands decreased drastically with increasing Ni content. The peak frequencies of the lower and upper bands were up- and down-shifted, respectively. The layered α-$NaFeO_2$-type ($R\bar{3}m$) structure is a rhombohedral superstructure of the rock-salt ($Fm3m$) structure. The cubic rock-salt structure exhibits only a single T1u IR-active mode, but has no Raman active mode. A reduction in rhombohedral distortion would degenerate the A1g and Eg modes of $R\bar{3}m$ into a T2g mode, which is not a vibrational mode of the rock-salt ($Fm3m$) structure. Hence, the observed changes, the decrease in intensity and the peak shifts, are attributable to a reduction in rhombohedral distortion by increasing Ni content.[5]

Another reason for the decrease in intensity is an increase in electrical conductivity. It was reported that the electrical conductivity of $LiNiO_2$ is better than that of $LiCoO_2$ because of their electronic structures.[6] Hence, the electrical conductivity of $LiCo_{1-y}Ni_yO_2$ is considered to increase with increasing Ni content. An increase in electrical conductivity reduces the optical skin depth of the incident laser beam from the surface of specimens, resulting in a decrease in Raman scattering intensity. Unfortunately, it is not clear at the present stage which factor plays a predominant role in the observed change in intensity.

It is known that the stoichiometric $LiNiO_2$ is difficult to obtain because high-temperature treatment of $LiNiO_2$ leads to a decomposition to $Li_{1-x}Ni_{1+x}O_2$ that has a partially disordered cation distribution.[4,7] Although the chemical compositions of our samples have not been determined yet, they would have had disordered cation distribution. Such disordered structure also should be considered to explain the observed Raman spectral changes in more detail.

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