Temperature and laser power dependencies of $LiCoO_2$ Raman spectra

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Raman spectroscopy is actively used to study the phase and structural changes in lithium-ion batteries electrode materials, since the low weight of lithium ions makes it difficult to quantitatively analyze materials by such methods as X-ray diffraction analysis and energy-dispersive X-ray spectroscopy. Thus, Raman spectrum of lithium cobalt oxide $LiCoO_2$ (LCO), clearly shows a shift of the bands towards lower wavenumbers with a decrease in their amplitude and broadening with deintercalation of lithium ions. A similar behavior of vibrational modes in the spectrum is also observed in the process of heating. Thus, the interpretation of the spectrum of a delithiated sample may be inaccurate, especially due to the possible laser heating of the LCO during measurements.

In this work, we investigated the features of the interaction of laser radiation with individual LCO particles. To do this, we first studied the temperature dependence of the parameters of the LCO Raman spectrum and found that the band shift is described by thermal expansion and anharmonicity. Next, we measured the dependence of the Raman spectrum parameters on the power of laser radiation. The results showed that the shift is more pronounced than during heating and can reach up to 22 cm^{-1} for the E_g and up to 20 cm^{-1} for the A_{1g} mode. In this case, the shift and broadening of the bands turned out to be inhomogeneous for different particles. Using the obtained ratio of the band shift versus temperature for the power dependence, we found that such a maximum shift is equivalent to the shift upon heating to approximately 900°C. Since LCO begins to form cobalt oxide at even lower temperatures, this suggests that this shift cannot be explained by laser-induced heating alone.

The results obtained indicate that, in Raman measurements of LCO, it is necessary to use a low excitation power to avoid degradation of the material and to consider laser heating in the quantitative analysis of the obtained experimental data.

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