

RAMAN SCATTERING IN LITHIUM INTERCALATED COMPOUNDS

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Abstract: A series of $\text{Li}_x\text{Co}_{0.9}\text{Ga}_{0.1}\text{O}_2$ oxides, for $0.3 \leq x \leq 1.0$, were obtained by us in using the carbonate process. A detailed analysis of the Raman spectra performed for these compounds and comparison with results for a number of oxides points to the formation of an additional phase of Co_3O_4 in the powder. It is possible that one such phase affects the electrochemical performance of the electrode

Lithium intercalated compounds have been used as the cathode active material for commercial rechargeable Li-ion batteries [1,2]. In this context the Li_xCoO_2 can be considered as the positive material more studied in the last years. Stoichiometric LiCoO_2 is a semiconductor at room temperature and its electrical conductivity increases with the removal of lithium ions to become metallic at $x \leq 0.2$ [3]. The capacity predicted for this material was never fully attained due to structural degradation during lithium extraction. In the attempt to enhancing the practical capacity and stabilizing the layered structure, several investigations of isostructural $\text{LiCo}_{1-y}\text{M}_y\text{O}_2$ compounds, were performed, for metals ions M such as nickel, manganese, chromium, aluminium, boron, rhodium or iron (see citations in ref. [4]). However the capacity output was found to decrease instead [4], and just marginal success toward increasing the electrochemical performance was found for a few dopants. Even though, the overall capacity may be reduced due to metal substitution the doped materials attain thermal stability in the delithiated state and a low capacity fade when cycled to high potentials [5]. From this point of view, the alternative dopants are attractive for battery applications. It has been recently found, that by Ga doping the LiCoO_2 compound may result in its improved electrochemical performance during overcharge [6]. Therefore, it is of fundamental importance to carry out a detailed investigation of the spectroscopic behavior of $\text{Li}_x\text{Co}_{0.9}\text{Ga}_{0.1}\text{O}_2$ for lithium spanning the whole range of deintercalation.

A series of $\text{Li}_x\text{Co}_{0.9}\text{Ga}_{0.1}\text{O}_2$ oxides, for $0.3 \leq x \leq 1.0$, were obtained by us in high temperature, (HT), and low temperature, (LT), conditions using the carbonate process. Raman spectra were performed for these compounds as well as for a number of related oxides. The HT- $\text{LiCo}_{0.9}\text{Ga}_{0.1}\text{O}_2$ spectrum was found to consist of two Raman bands at 486 cm^{-1} and 595 cm^{-1} , corresponding to the E_g and A_{1g} symmetries of the $R3m$ factor group, respectively. No differences in peak position were found as compared with the Raman spectrum of LiCoO_2 . The delithiated sample HT- $\text{Li}_x\text{Co}_{0.9}\text{Ga}_{0.1}\text{O}_2$, with $x = 0.3$, spectrum is show in Fig. 1 (a) lowest profile. The spectrum shows an additional structure peaking at 674 cm^{-1} . Also shown in this figure are the spectra for the pristine LT- $\text{LiCo}_{0.9}\text{Ga}_{0.1}\text{O}_2$ and that of Co_3O_4 . The isostructural LT- LiCoO_2 is known to crystallise in the spinel structure with space group $Fd3m$, and contains four molecules in the Bravais cell. Factor group analysis predicts four Raman bands for the crystal [7]: $A_{1g} + E_g + 2F_{2g}$. Figure 1 (a) shows at least one additional peak at about 670 cm^{-1} . Comparison of these spectra allows to assign the peaks in addition to those predicted by factor group analysis as the most intense Raman peak of Co_3O_4 . The differences in position observed are typical of strained grains. Figure 1 (b) shows the spectra for progressive delithiation of the HT- $\text{LiCo}_{0.9}\text{Ga}_{0.1}\text{O}_2$. It can be observed in this figure that by removing Li great changes in the Raman spectrum occur, with a drastic decrease in intensities and the appearance of new peaks at about 520 cm^{-1} and 680 cm^{-1} . For samples with increased

delithiation, these new structures gain intensity in a systematic way. For the higher delithiation achieved here, $x = 0.3$, the dominant structure in the spectrum is the 680 cm^{-1} band. A detailed analysis and comparison with results for a number of oxides points to the formation of an additional phase in the powder corresponding to the Co_3O_4 oxide. This oxide together with the original compound do not form a homogeneous mixture. It is possible that one such impurity phase affects the structural stability of the electrode and the electrochemical performance in consequence.

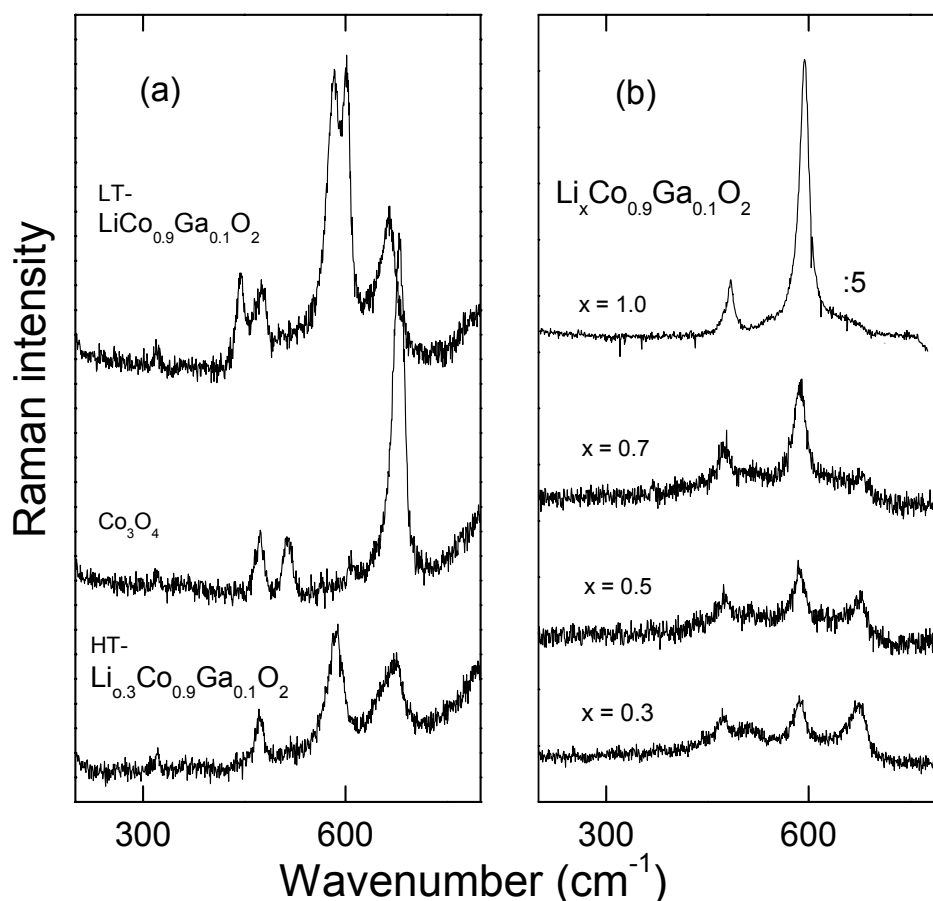


Fig. 1. (a): Raman spectrum of the LT- $\text{LiCo}_{0.9}\text{Ga}_{0.1}\text{O}_2$, Co_3O_4 , and HT- $\text{Li}_{0.3}\text{Co}_{0.9}\text{Ga}_{0.1}\text{O}_2$.
(b): Raman spectrum of $\text{Li}_x\text{Co}_{0.9}\text{Ga}_{0.1}\text{O}_2$ for $x = 1.0, 0.7, 0.5$ and 0.3 , respectively.

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