Infrared Spectroscopic Study of LiCoO$_2$ Thin Films

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Site disorder of Co^{3+} ions in sputtered films of lithium cobaltite has been examined using infrared spectroscopy. Both transmission and reflectance modes have been used to characterize the nature of IR absorption. It is found that Co^{3+} in the sputtered films occupy two types of octahedral sites that differ in the nature of second-neighbor environment. Li^{+} ions exhibit two bands, which may arise from tetrahedral and octahedral site occupancies or from the presence of disordered regions in the films. © 2002 Elsevier Science (USA)

INTRODUCTION

There is a growing interest in lithium battery materials (1) in view of the definitive advantages of a lithium battery, namely, high voltages and high power densities (2, 3). Lithium cobaltite (LiCoO$_2$) has a great potential for use as electrode material (for batteries with an operating potential of ~ 4 V and power density ~ 140 mA/g) (4–6). LiCoO$_2$ has a layered rocksalt structure (4, 7) and Li^{+} ions can be deintercalated reversibly to a very high extent (up to 80%) and with good cyclability (8, 9). However, it has been noted that LiCoO$_2$ prepared by different methods exhibits significant differences in its electrode behavior (10–12). Although electrode materials synthesized at low temperature exhibit better cyclability, the nature of the site occupied by lithium has been found to be altered significantly during cycling, which affects the cell capacity (13). It has been reported that as-synthesized (low-temperature method) LiCoO$_2$ (LT-LiCoO$_2$) consists of approximately 6% Co^{3+} ions located in the lithium layer in lithium ion sites (13, 14). A similar percentage of lithium ions is likely to be present in the cobalt layer or is otherwise (necessarily) located in tetrahedral sites in the structure. Whether this interchange in site occupation induces preferential occupation of tetrahedral sites by other Li^{+} ions during intercalation–deintercalation cycles has not

been investigated. Raman spectroscopic studies, however, indicate that Co^{3+} ions occupy only one type of sites (15). During electrochemical cycling not only has mixing in both Li^{+} and Co^{3+} layers been observed due to the appearance of $\{10\bar{1}0\}$ reflections in electron diffraction but also the formation of spinel structures due to the appearance of $\{220\}$ reflections (6). The structure of LiCoO$_2$ thin films used as electrodes in battery applications is by comparison even less understood. Polo da Fonseca *et al.* (16) found that as-sputtered thin films are amorphous, but do begin to crystallize into two phases, LiCoO$_2$ and Li$_{1.47}$Co$_3$O$_4$, the latter being a spinel. Their infrared studies indicate the presence of a peak at 460 cm^{-1} due to tetrahedral Li^{+} ion in addition to three other peaks due to [CoO$_6$] octahedra. In related studies from this laboratory (17), sputtered thin films of LiCoO$_2$ have been found to be X-ray amorphous even after annealing at 700°C, but high-resolution electron microscopy (HREM) has revealed that the structure of the film consists of a two-dimensional mosaic of highly crystalline nanodomains with amorphous boundaries. In such a structure, the site preference of Li^{+} ion can be quite different compared to bulk crystalline cobaltite. Further, the sputtered film of the cobaltite should be expected to be structurally similar to HT-LiCoO$_2$, which is prepared at high temperatures compared to LT-LiCoO$_2$ prepared at low temperatures. Also, the sputtered cobaltite films are prone to exhibit a significant degree of non-stoichiometry in view of the variable valency of cobalt.

Therefore, we consider it important to examine the structural aspects of LiCoO$_2$ thin films, using spectroscopic methods, which reveal the site occupancies of cobalt and lithium. Infrared spectroscopy serves this purpose well because both cobalt and lithium ions are present in oxygen polyhedra in the structure and give rise to characteristic absorption features in vibrational spectra. The spectroscopic features are also quite distinct for tetrahedral and octahedral site occupancies in oxide matrices. In this paper we report on and discuss the IR spectroscopic investigations of LiCoO$_2$ both in bulk and in thin

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film forms, the latter prepared by sputtering from $LiCoO_2$ targets. $LiCoO_2$ itself has been prepared by the high-temperature route. We have also examined the IR spectra of Co_3O_4 and Li_2CO_3 in order to make necessary comparisons.

EXPERIMENTAL

HT-$LiCoO_2$ has been synthesized by heating a mixture of lithium carbonate and Co_3O_4 at 900°C in an oxygen atmosphere. Co_3O_4 is prepared from cobalt nitrate by heating to 400°C in an oxygen atmosphere. The crystal structures of HT-$LiCoO_2$ and Co_3O_4 have been confirmed using X-ray diffraction. Transmittance spectra of crystalline HT-$LiCoO_2$ have been obtained both in KBr and in polyethylene pellets using a FTIR spectrometer (Perkin-Elmer PE 983). Specular reflectance measurements have been made on pellets of HT-$LiCoO_2$ powders using a Nicolet 20 F spectrometer at a resolution of $8 \, cm^{-1}$.

Amorphous thin films of lithium cobalt oxide have been deposited by RF magnetron sputtering using HT-$LiCoO_2$ pellets as target, on silicon wafer substrates. Argon or a mixture of argon and oxygen (for reactive sputtering) has been used as discharge gas. Details of the deposition process and target preparation have been described elsewhere (18). The amorphous thin films have been heated at 350, 600, and 750°C for 30 min each in an oxygen atmosphere. The IR spectra of the films have been corrected for the silicon (substrate) spectrum. The transmittance spectra have been recorded in the range of 2000–15 cm^{-1} using a Perkin-Elmer PE983 spectrometer.

RESULTS AND DISCUSSION

The IR spectrum (in the range of 800–400 cm^{-1}) of HT-$LiCoO_2$, used as the target material for thin film preparations, obtained in KBr pellets is shown in Fig. 1a. The choice of the range was made in view of the fact that KBr itself has no absorption in this region. There are two prominent peaks at 530 and 600 cm^{-1} and a prominent shoulder around 670 cm^{-1}. The 600-cm^{-1} peaks is quite broad. The spectrum has been deconvoluted approximately using four Gaussians in the region of 450–700 cm^{-1} and shown in Fig. 1b, which supports the assumption of the presence of an absorption peak at $\sim 575 \, cm^{-1}$. A specular reflection spectrum obtained from pellets of HT-$LiCoO_2$ is presented in Fig. 2a. The spectrum presented in Fig. 2b has been simulated using the standard procedure based on the use of product dielectric constants (19). Simulation data reveal the presence of three longitudinal optical modes at 690, 560, and 290 cm^{-1} respectively and three transverse optical modes at 590, 550, and 260 cm^{-1} respectively. In $LiCoO_2$, which is a layered oxide with a rock salt structure, Li^+ and Co^{3+} ions (ideally) occupy octahedral sites in

(a)

(b)

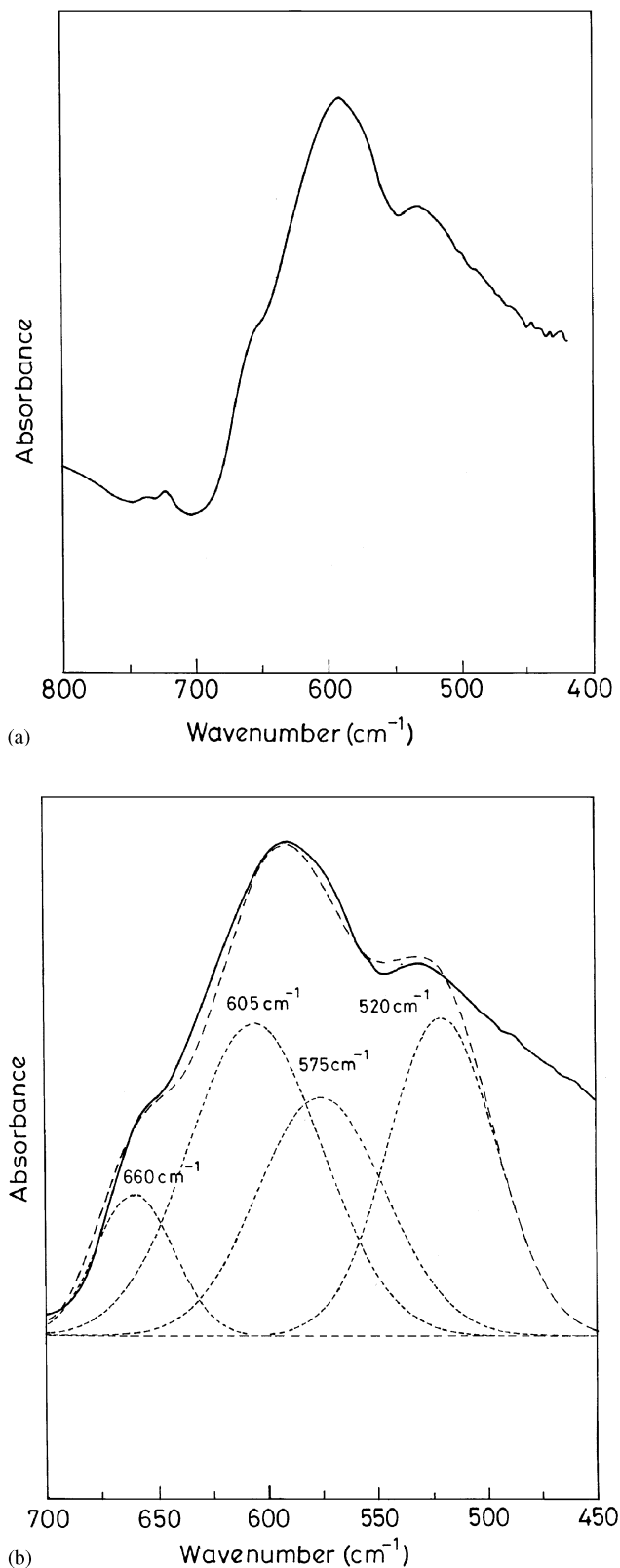**FIG. 1.** (a) KBr spectrum of HT-$LiCoO_2$, and (b) (approximate) deconvolution of the region between 450 and 700 cm^{-1} with the use of four Gaussians.
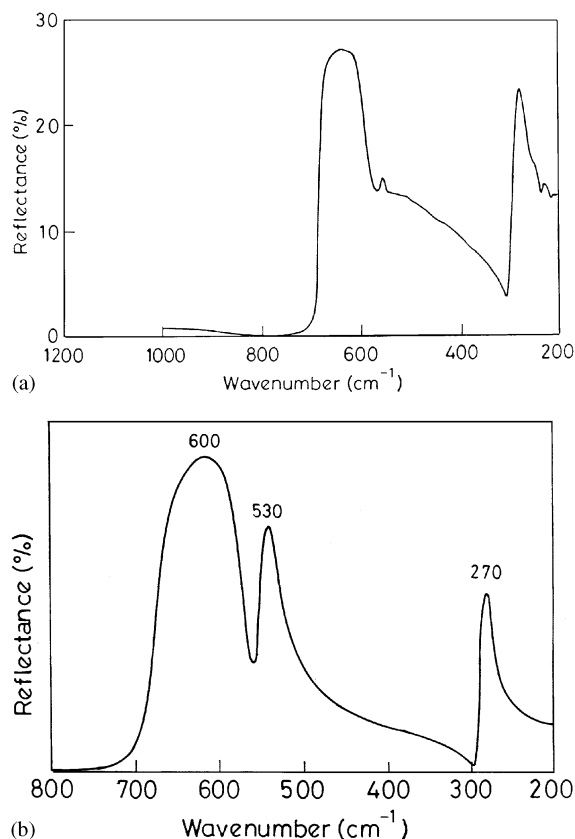
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FIG. 2. (a) IR Reflectance spectrum of HT-LiCoO$_2$, and (b) theoretically simulated spectrum.

alternate (111) layers. For the octahedral site occupation (O$_h$), there are only two IR active modes (20). It was noted by Tarte and Preudhomme (21) that isotopic substitution of lithium in LiCoO$_2$ shifts the low-frequency mode significantly without affecting the ~600-cm^{-1} absorption. Therefore, the two low-frequency modes at 260 and 290 cm^{-1} may be associated with Li$^+$ ion vibrations. The other four frequencies are, therefore, associated with vibrational modes arising from CoO$_6$ octahedra. the presence of four absorption bands in the region above 400–700 cm^{-1} was already noted in the deconvoluted KBr spectrum of HT-LiCoO$_2$ in Fig. 1b as well. The intense and broad 600-cm^{-1} peak therefore consists of a buried peak at ~575 cm^{-1}. We consider both the reflectance spectra of fig. 2b and the deconvoluted spectra of fig. 1b as being indicative of the number of active absorption peaks present in the IR spectra. This is because analysis of reflectance spectra involves simulation with adjustable parameters. Also the best fit spectrum in Fig. 2b involves a large peak at 530 cm^{-1}, not seen so clearly in Fig. 2a. Similarly deconvolution has been done with only a part of the spectrum and absorption on the low-frequency side is quite high.

Therefore, we infer that there are four absorption peaks at approximately 660, 605, 575, and 520 cm^{-1} frequencies, which are attributable to vibrations arising from [CoO$_6$] units. since there can be only two IR active absorptions of octahedral [CoO$_6$] units the spectra indicate the presence of two different types of octahedral sites occupied by Co^{3+} ions in HT-LiCoO$_2$. It also immediately suggests that as in Lt-LiCoO$_2$, there is a site occupancy disorder in HT-LiCoO$_2$ also. A significant fraction of Co^{3+} ions may, therefore, occupy octahedral sites present in the lithium layer. We may distinguish the spectral features of the Co^{3+} ion sites as follows.

There are two features of lithium layer sites, which affect the IR spectra of Co^{3+} ions occupying them. First, the second-neighbor environment of Co^{3+} in the Li$^+$ layers is largely Li$^+$, and it reduces the coulombic repulsive interaction (Co^{3+}–Li$^+$ compared to Co^{3+}–Co^{3+}). Secondly, the site is more distorted, because of the dissimilarity of both charge and size (of Co^{3+} ions) in comparison to those of the Li$^+$ ion to which the site belongs. Therefore, the [CoO$_6$] octahedra in the Li$^+$ layer have a higher cohesive energy. Hence, we associate the higher absorption frequencies at 660 and at 575 cm^{-1} to Co^{3+} ions in the lithium layers. The peaks at 605 and 520 cm^{-1} are, therefore, associated with Co^{3+} in its own site.

The IR spectrum of Co$_3$O$_4$, which is a spinel, has also been investigated in this context. Co^{3+} ions in Co$_3$O$_4$ occupy octahedral sites, but the Co^{2+} ions occupy only the tetrahedral sites. The two IR active vibrations of Co^{3+} have been found to occur at 655 and 555 cm^{-1}, while those of Co^{2+} in tetrahedral sites appear at 390 and 215 cm^{-1} (in the T_d symmetry also there are only two allowed IR vibrations). The assignment of these absorptions as due to Co^{2+} vibrational frequencies in the tetrahedral sites is well supported by the earlier work of Kozlova and Shub (22). The differences of Co^{3+} related frequencies between Co$_3$O$_4$ and HT-LiCoO$_2$ can be attributed to the differences in the second-neighbor environment in the two materials. While the second neighbors of Co^{3+} in Co$_3$O$_4$ consist of Co^{2+} ions, only Li$^+$ ions are present in HT-LiCoO$_2$. The higher charge on Co^{2+} than on Li$^+$ destabilizes (higher Co^{3+}–Co^{2+} repulsion) the [CoO$_6$] octahedra in Co$_3$O$_4$ more than Li$^+$ does in LiCoO$_2$. This causes the higher frequency (655 cm^{-1}) in Co$_3$O$_4$ to be somewhat lower than that in LiCoO$_2$ (670 cm^{-1}). These assignments are consistent in the sense that the three types of Co^{3+} sites, namely (a) Co^{3+} with Co^{3+} as second neighbor as in layered LiCoO$_2$, (b) Co^{3+} with Co^{2+} as second neighbor as in Co$_3$O$_4$, and (c) Co^{3+} with Li$^+$ as second neighbor as in the "wrong" sites of LiCoO$_2$, all in octahedral sites, give rise to the frequency pairs (600, 530 cm^{-1}), (655, 555 cm^{-1}), and (670, 580 cm^{-1}) respectively in which there is systematic variation of the frequencies. The IR absorption intensities (or extinction

coefficients) are very sensitive to the extent of distortion in the octahedral sites and hence to the dipole strength (23). However, making a quantitative comparison of absorption intensities has not been possible with the present data.

The IR absorption bands due to Li$^+$ vibration in oxide ion cages are generally very broad (24,25) and particularly so in amorphous materials (26) in which the full-width-at-half maximum (FWHM) of these peaks are sometimes nearly of the same magnitude as the absorption frequencies Li$^+$ ions in oxygen cages of tetrahedral symmetries always give rise to absorption bands in the region of 400 cm^{-1}. As reported by Rao et al. (24), this absorption band does not appear to be sensitive to the chemical nature of oxygens forming the cage, because Li$^+$ in carbonates, ferrites, silicates, titanates, and even organic complexes, where it is coordinated to four oxygens in tetrahedral symmetry, gives rise to peaks of roughly similar frequency. That the ~400-cm^{-1} band arises only from Li$^+$ vibrations in tetrahedral sites has been ascertained neatly by studying the isotope effect in lithium carbonate by Tarte and Preudhomme (21). Absence of these peaks in the spectra of HT-LiCoO$_2$ rule out the present of Li$^+$ in tetrahedral symmetries much unlike in LT-LiCoO$_2$ where these absorptions are seen. Therefore, the Co^{3+} ions present in the Li$^+$ layer have either displaced Li$^+$ ions to some extended lattice position of octahedral symmetry or have exchanged positions with them. Thus, the conclusions drawn by Montoro et al. (31) regarding the absence of disorder in Co^{3+} positions are not supported by the present observations.

The focus of this work is the IR spectroscopy of sputtered thin films of LiCoO$_2$, and their IR spectra are shown in Fig. 3. In Fig. 3a is the spectrum of the unannealed film, in while Fig. 3b is that of the film annealed at 600°C. The unannealed film has several vibrational features in the region above 700 cm^{-1}. The two major frequencies correspond to the vibrations of CO$_3^{2-}$ ion and are present around 900 and 1450 cm^{-1}, respectively. These are the bending and stretching modes of the carbonate (24, 27). They are caused by the chemisorption of CO$_2$ by the films, exposed to atmosphere. These CO$_3^{2-}$ ion features, however, disappear when the films are annealed. The major peak in the spectra of the unannealed film is centered around 520 cm^{-1} and it splits into several peaks, of which the important ones are those at 555, 460, and 260 cm^{-1} and the shoulders at 590, 630, and 615 cm^{-1}. There is also a minor absorption feature around 380 cm^{-1}. Several important spectroscopic changes occur below 650 cm^{-1} in the annealed films.

In order to examine them in detail, the films were further annealed at 750°C. The effects of annealing at lower and higher temperatures are presented together in Fig. 4. The somewhat featureless spectrum (a) of Fig. 4 is of the unannealed film. The evolution of vibrational features of cobalt–oxygen and lithium–oxygen polyhedra is revealed in
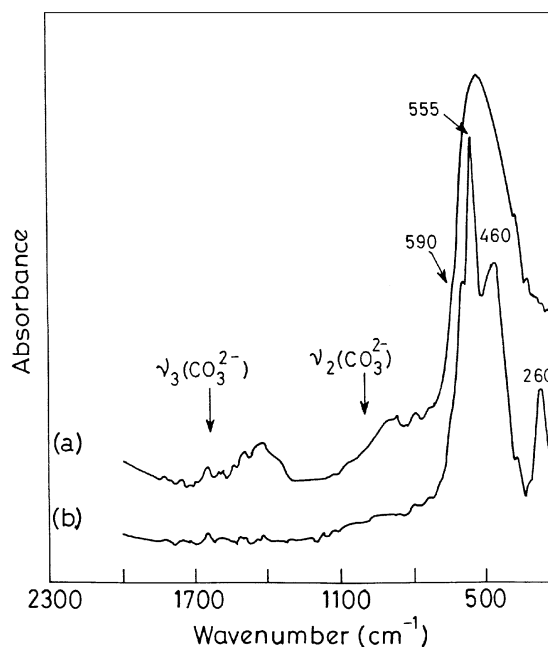

FIG. 3. IR absorption spectra of thin films (a) unannealed and (b) annealed at 600°C.
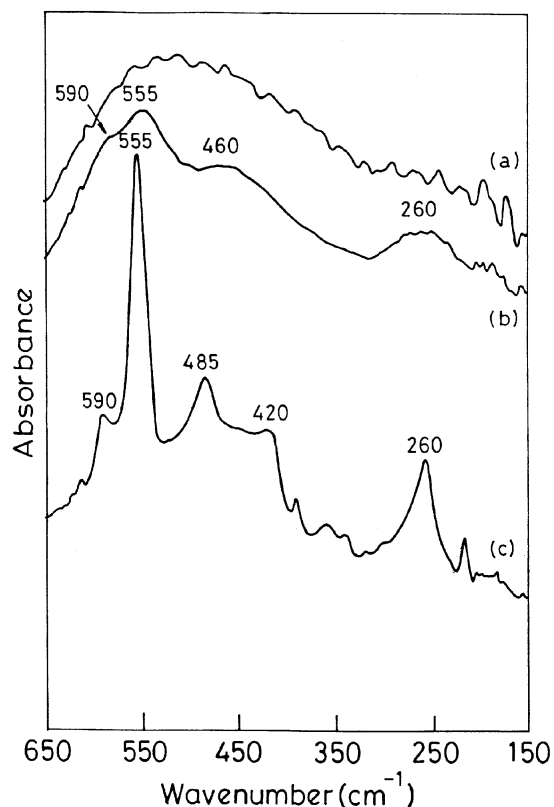

FIG. 4. IR absorption spectra in the region of 150 to 650 cm^{-1}: (a) unannealed film, (b) annealed at 350°C, and (c) annealed at 750°C.

spectrum (b) even as the film is annealed only at 350°C. The high-temperature (750°C) annealed film develops several IR absorption peaks and are marked in curve (c) of Fig. 4. The observed IR frequencies of bulk HT-LiCoO$_2$ and those of sputtered films can be correlated and the correlations are listed in Table 1. It would be perhaps be equally satisfactory to assign 555 and 485 cm^{-1} bands to Co^{3+} in its own sites and the combinations of 615 and 590 cm^{-1} bands to Co^{3+} in the Li$^+$ layers (wrong site) (28).

The data in Table 1 is clearly indicative of the presence of both types of Co^{3+} ions in the crystallized films—Co^{3+} ions in their own sites in the LiCoO$_2$ structure and Co^{3+} ions in the Li$^+$ ion positions. The frequencies in the film are, however, shifted slightly to higher energies, indicative of a further decrease in the interlayer or interoctahedral repulsion. In addition to Li$^+$ ion vibrations in tetrahedral sites there are IR peaks of Li$^+$ ion vibrations (<300 cm^{-1}) in octahedral positions.

Therefore, both the layer rock salt crystal structure and the interlayer exchange disorder of Li$^+$ and Co^{3+} ions of LiCoO$_2$ seem to be present in the sputtered films also to a significant extent. All the frequencies below 500 cm^{-1} must be attributed only to Li$^+$ ions because, in these films which have been annealed in air under highly oxidizing conditions, it is reasonable to assume that Co^{2+} ion are absent. Also, the composition of these films clearly reveals oxygen excess nonstoichiometry, which is discussed elsewhere (17). Therefore absorption features at <500 cm^{-1} confirm the presence of Li$^+$ ions in both tetrahedral and octahedral symmetries; Li$^+$ ions give rise to IR absorptions between 390 and 485 cm^{-1} due to tetrahedral Li$^+$ occupancies and between 260 and 215 cm^{-1} due to octahedral Li$^+$ occupancies.

Since the films were crystallized from the amorphous state, it would be of interest to take into consideration spectroscopic features germane to disordered solids. It is well known in glasses that the IR spectra due to Li$^+$ ions occur in the same region (around 250 and 400 cm^{-1}) but are attributed to two different populations of lithium ions

present in differing environments and not to geometries of occupied sites (26). It is our suspicion that such a situation is likely to be present in the 750°C annealed thin films, because of the following reasons. We have noted elsewhere (17) that these annealed films actually correspond to a mosaic of crystalline domains whose linear dimensions are roughly 10 nm. We should like to consider that the interface between these domains continues to remain amorphous. The interfacial region and the junctions together constitute an about 1-nm-thick boundary around each domain of roughly 10 nm size. This is quite reminiscent of a cluster-tissue texture of glasses (29, 30) and now manifests in two-dimensional films. A fraction of the area (and also the volume) of the disordered tissue-like region would be $\sim (11^2–10^2)/10^2 \sim 20\%$. In comparison with crystalline domains, the volume ratios of the amorphous to crystalline areas would be $\sim 0.2/0.8 \sim 0.25$. We should, therefore, expect about 25% of lithium to be present in such areas, CoO$_6$ units may still retain there octahedrality in the tissue region also merely by virtue of a larger charge ($+3$) on them, and they do not alter the spectroscopic features much. The spectral features due to Li$^+$ ions in the amorphous region, therefore, cannot be strictly associated with tetrahedral or octahedral sites— they represent a variety of sites failing into two distinct but broad populations.

The absence of any alteration of the spectroscopic features and hence of the valence state of Co^{3+} is very interesting. When this is viewed together with the observation that these films have an oxygen excess, it appears that a good fraction of oxygen atoms are present not as O^{2-} but as O$^-$. In their X-ray absorption study of deintercalated LiCoO$_2$, Monatoro et al. (31) have observed that the valence state of Co^{3+} does not change, while that of oxygen indeed is reduced. Koyama et al. (32) have arrived at a similar conclusion from their discrete variational Xα calculation of LiCoO$_2$ clusters. In fact vibrational features attributable to [Co^{IV}O$_6$] octahedra have not been found in the present IR spectra.

We may also further recall here that the lithium ion vibrations in tetrahedral occupancy in crystalline materials which occur at ~ 400 cm^{-1} are also unaltered by the chemical nature of the cage oxygen (24). Therefore, we suggest that both Co^{3+} and Li$^+$ ions in the tissue are coordinated to oxygen ions of lower charge like O$^-$ rather than O^{2-}. This will lead to excess oxygen nonstoichiometry and to interesting electrical properties of the films, which is discussed separately (17). One obvious situation may be noted here for interest, and that is when the entire 20% of the material in the interfacial region is considered as singly charged oxygen (this may require coordination polyhedra to be largely in corner sharing rather than in edge-sharing configuration, the latter being the situation in the crystalline LiCoO$_2$), then $0.2 \times 2 = 0.4$ moles of oxygen can be

TABLE 1
Correspondence of Frequencies (cm^{-1})

HT-LiCoO$_2$	Thin film	Assignment
660	630 (W)	Co^{3+} in Li$^+$ layer in octahedral sites.
575	590	
605	615 (W)	Co^{3+} in Co^{3+} layer in octahedral sites.
520	555	
—	485	Li$^+$ in tetrahedral sites.
	420	
	390	
<300	260	Li$^+$ in octahedral sites.
(not shown in Fig. 4)	215	

added to the system to increase oxygen nonstoichiometry to $LiCoO_{2.4}$.

SUMMARY AND CONCLUSIONS

Infrared spectra of lithium cobaltite thin films sputtered from HT–$LiCoO_2$ targets have been studied. It is found that Co^{3+} is present in two different octahedral sites, the second type of sites being Li^+ ion sites with which Co^{3+} has exchanged positions. Li^+ ions cause two major absorptions in the region $< 500 \, cm^{-1}$ that may be either due to the presence of Li^+ in tetrahedral and octahedral sites or due to two different populations of Li^+ ions associated with the interdomain amorphous regions.

ACKNOWLEDGMENTS

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