

# Structure and optical absorption of combustion-synthesized nanocrystalline LiCoO<sub>2</sub>

Paromita Ghosh, S. Mahanty, M.W. Raja, R.N. Basu,<sup>a)</sup> and H.S. Maiti

Fuel Cell and Battery Section, Electroceramics Division, Central Glass and Ceramic Research Institute, Kolkata 700 032, India

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Nanocrystalline LiCoO<sub>2</sub> powders (10–50 nm) were synthesized by a citrate-nitrate combustion process followed by calcination at different temperatures (300–800 °C) in air. Thermogravimetric analyses indicated a sharp combustion at a low temperature of 225 °C, producing fine crystallites. Quantitative phase analyses from the x-ray diffractograms showed that while annealing at 500 °C produced mixed phases of cubic and rhombohedral LiCoO<sub>2</sub>, annealing at 800 °C resulted in single-phase rhombohedral LiCoO<sub>2</sub>. Electronic transitions related to the Co 3d bands were investigated by ultraviolet-visible reflectance spectra in absorbance mode and were ascribed to the Co 3d intra-band transition involving  $t_{2g}$  and  $e_g$  orbitals. The  $d-d$  transitions underwent a blue shift of about 0.3 eV as the cubic LiCoO<sub>2</sub> transformed into the rhombohedral structure with band gap values of about 1.4 and 1.7 eV.

## I. INTRODUCTION

In recent years, extensive research has been focused on LiCoO<sub>2</sub> for cathode materials in lithium ion secondary batteries because it possesses a high cell voltage of about 4 V, high charge capacity of around 120 mAhg<sup>-1</sup>, a long cycle life, and a low self discharge.<sup>1–3</sup> Understanding the electronic structure and the electronic processes involved in Co 3d bands in LiCoO<sub>2</sub> is a very crucial issue as most of its electrochemical properties would be affected by the electronic structure. Depending upon the temperature, LiCoO<sub>2</sub> exists in two crystalline forms: a low-temperature (LT) (<500 °C) cubic spinel (space group  $Fd\bar{3}m$ ) and a high-temperature (HT) (>500 °C) layered rock-salt structure (space group  $R\bar{3}m$ ), commonly known as LT and HT LiCoO<sub>2</sub>, respectively, in the literature.<sup>4–12</sup> Both structures are based on the same oxide sublattice (a cubic close-packed oxygen network) but differ essentially in the spatial arrangement of the cations. The cubic phase of LiCoO<sub>2</sub> is characterized by a random distribution of cobalt and lithium cation layers of about 75% Co and 25% Li (Co-rich layer) alternating with cation layers of about 25% Co and 75% lithium (Li-rich layer) whereas the rhombohedral phase is distinguished by an ideal rocksalt  $\alpha$ -sodium ferrite ( $\alpha$ -NaFeO<sub>2</sub>) structure showing alternating layers of Li and Co.<sup>12</sup> The layered rock-salt form of LiCoO<sub>2</sub> consists of slightly distorted CoO<sub>6</sub> octahedra; thus a ligand field is strong

enough to stabilize a Co<sup>3+</sup> low-spin ground state, and hence, all six 3d electrons of Co<sup>3+</sup> have a low-spin configuration.<sup>13,14</sup> Co 3d bands of layered rock-salt LiCoO<sub>2</sub> consist of three  $t_{2g}$  (valence band) and two  $e_g$  (conduction band) levels. The crystal structure of Co<sub>3</sub>O<sub>4</sub> represents a normal spinel structure with Co<sup>2+</sup> ions occupying tetrahedral sites with lower  $e_g$  and higher  $t_{2g}$  orbitals and Co<sup>3+</sup> ions occupying octahedral sites with lower  $t_{2g}$  and higher  $e_g$  orbitals in the ligand field of oxygen ions.<sup>4,8</sup> Although, like Co<sub>3</sub>O<sub>4</sub>, cubic LiCoO<sub>2</sub> has a normal spinel structure, recent studies by Shao-Horn et al.<sup>15</sup> using electron diffraction show that the cation distribution is different in LiCoO<sub>2</sub> such that only Co<sup>3+</sup> ions are present in the octahedral sites, though the possibility of some minute Co<sup>2+</sup> defects residing in the tetrahedral sites cannot be completely ruled out. Therefore, while the conduction band in the case of Co<sub>3</sub>O<sub>4</sub> is formed by the hybridization of four empty  $e_g$  (Co<sup>3+</sup>) and three  $t_{2g}$  holes (Co<sup>2+</sup>),<sup>16</sup> the conduction band of cubic LiCoO<sub>2</sub> is formed by the four empty  $e_g$  holes alone. Aydinol et al.<sup>13</sup> found a value of ~2.2 eV for the  $t_{2g}$ - $e_g$  separation from the band-structure calculations of LiCoO<sub>2</sub> using the ab initio pseudopotential method and ascribed it to a downshift of the  $e_g$  density of states in comparison to CoO (~2.3 eV) due to an increase in Co–O bond length resulting from Li incorporation into CoO. On the other hand, Czyzyk et al.<sup>14</sup> performed the calculations by the localized spherical wave (LSW) method and predicted a value of 1.7 eV. Elp et al.<sup>16</sup> investigated the electronic structure of LiCoO<sub>2</sub> by x-ray photo electron spectroscopy (XPS) and Bremsstrahlung isochromat spectroscopy (BIS) and reported a band gap of 2.7 eV. After a few years, Rosolen et al.<sup>17</sup>

<sup>a)</sup>Address all correspondence to this author.

e-mail: [rnbasu@cgcri.res.in](mailto:rnbasu@cgcri.res.in)  
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observed that the Co–O bond length increases from 1.905 to 1.933 Å for Li<sub>0.5</sub>CoO<sub>2</sub> to LiCoO<sub>2</sub>, and from the photocurrent spectra studies, the authors estimated a band gap of 2.5 eV. These studies show a considerable spread in the band gap value of LiCoO<sub>2</sub>, both in theoretical calculations and in experimental results (1.7–2.5 eV).

Recently, Kushida et al.<sup>5,18</sup> used ultraviolet-visible (UV-vis) spectroscopy to study the electronic transitions in layered rhombohedral LiCoO<sub>2</sub> by depositing thin films onto Si or SiO<sub>2</sub> substrates. They observed a prominent absorption peak at ~2.1 eV, which was attributed to the *d-d* transition. However, polycrystalline thin films always show a higher band gap value compared to the bulk powder or single-crystal materials. Moreover, as the actual electrodes are made out of bulk powder, it seems necessary to experimentally investigate the *d-d* transition processes in bulk LiCoO<sub>2</sub> in more detail both in the rhombohedral and the cubic form. Hence, with this objective in mind, in the present work, the phase transformation and the associated optical transitions in each phase were studied systematically for combustion-synthesized LiCoO<sub>2</sub> powder samples.

## II. EXPERIMENTAL

LiCoO<sub>2</sub> powders were synthesized through a conventional citrate-nitrate gel combustion process.<sup>19</sup> An aqueous solution of lithium nitrate (LiNO<sub>3</sub>), cobaltous nitrate hexahydrate [Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O] (s.d. fine Chemicals, India, 99.5%) and citric acid monohydrate (Merck, India, 99.0%) was heated on a hot plate at a temperature of ~150 °C. Citric acid was added in required quantities to control the citrate-to-nitrate (C/N) ratio. Citric acid acted both as a fuel for the combustion process as well as a chelating agent for the metal ions (Li<sup>+</sup> and Co<sup>++</sup>) in solution. The homogeneity of the solution was ensured by constant stirring of the solution by a magnetic needle. The heating was continued until the clear dark purple solution turned into a viscous gel and ultimately burned into a black mass containing the precursor metal oxides for the formation of LiCoO<sub>2</sub>. The as-synthesized LiCoO<sub>2</sub> powder was collected and subjected to further heat treatment in air at three different temperatures, 300, 500, and 800 °C, for a period of 5 h. These three samples are henceforth referred to as C3, C5, and C8, respectively, and the as-synthesized powder is referred to as C.

Thermogravimetric analyses (TGA) of the gel and the as-synthesized powder sample were performed in the temperature ranges 30–600 °C and 30–1000 °C, respectively, by a Shimadzu Thermal Analyzer (Model TA-50, Japan) with a heating rate of 10 °C/min. X-ray powder diffractograms were recorded in the 2θ range 15–70° at a scanning rate of 2°/min by a Philips X'Pert x-ray diffractometer (The Netherlands) with Cu K<sub>α</sub> radiation at 40 KV and 40 mA. A slow scanning at a rate of 0.4°/min

in the 2θ range 55–75° was performed to allow clear observation of the splitting of the higher angle peaks characteristic of the rhombohedral phase. Rietveld refinement of the powder x-ray diffraction (XRD) profiles and quantitative phase analysis were carried out with the PANalytical Highscore Plus Program (PANalytical B.V., The Netherlands). The size-strain analysis was performed by comparing the XRD peak profile width to that of a standard silicon scan to account for the instrumental broadening. Fourier transform infrared spectroscopy (FTIR) was carried out in the wave number range of 2500–400 cm<sup>-1</sup> by a Nicolet 5 PC spectrometer (Thermo Fisher Scientific, Inc., US). The morphology of the samples was examined by a ZEISS Supra 35 (Germany) field emission scanning electron microscope (FE-SEM). Optical reflectance spectra in the absorbance mode of the samples were recorded in the wavelength range of 200–2000 nm using a Shimadzu UV3100 UV-vis spectrophotometer (Japan). For comparison, absorption spectrum for Co<sub>3</sub>O<sub>4</sub> was also recorded in the same wavelength range. Inductively coupled plasma (ICP) analyses of the LiCoO<sub>2</sub> samples were performed with a Spectro Flame ICP-AES Spectrometer (Germany).

## III. RESULTS AND DISCUSSION

Figure 1(a) shows the TGA plot of the gel. An initial weight loss was observed below 150 °C, which is due to the removal of the absorbed water.<sup>20</sup> At around 225 °C, a sharp weight loss of about 93% was observed, indicating instantaneous combustion, and could be related to the formation of LiCoO<sub>2</sub>. It was confirmed by quantitative phase analyses of the as-synthesized powder (sample C) that a considerable amount of CoO was present as a second phase along with LiCoO<sub>2</sub> in this sample. Among the oxides of cobalt, CoO is formed at temperatures above 800 °C.<sup>20</sup> Thus, the presence of CoO in the as-synthesized powder indicated that during combustion the flame temperature exceeded 800 °C. After 225 °C, except for a small weight gain of about 2% at ~280 °C, no

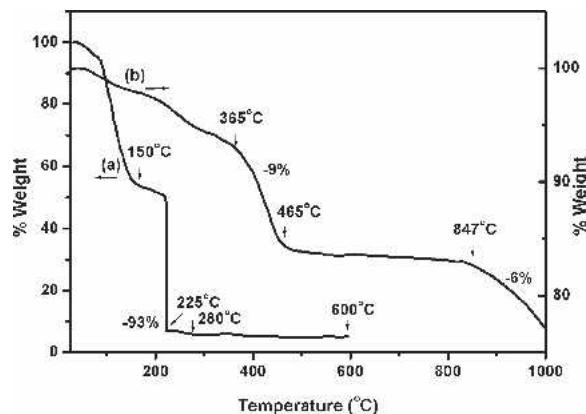


FIG. 1. TGA curves for (a) precursor gel and (b) as-synthesized LiCoO<sub>2</sub>.

TABLE I. Structural and optical results for the synthesized nanocrystalline LiCoO<sub>2</sub>.

Sample code	Calcination temperature (°C; time = 5 h)	Phases				Lattice parameters of LiCoO <sub>2</sub> (Å)		Crystallite size of LiCoO <sub>2</sub> (nm)	Band gap of LiCoO <sub>2</sub> phase (eV)
		LiCoO <sub>2</sub> (C)	Co <sub>3</sub> O <sub>4</sub> (C)	CoO (C)	LiCoO <sub>2</sub> (R)	<i>a</i> (±0.0002)	<i>c</i> (±0.0002)		
C	As-synthesized	46%	...	54%	...	8.0230	...	...	...
C3	300	46%	54%	...	...	7.9831	...	10	1.43
C5	500	15%	...	...	85%	2.8174	14.0229	19	1.69
C8	800	...	...	...	100%	2.8141	14.0433	51	1.68

further significant change in weight was observed up to 600 °C. This small weight gain may have been caused by the conversion of CoO to the low-temperature stable form, Co<sub>3</sub>O<sub>4</sub>, on heating.<sup>21</sup> Figure 1(b) shows the TGA curve of the as-synthesized powder (sample C). The curve consists of four segments: below 365 °C, a gradual weight loss was observed, which may have been caused by the removal of absorbed moisture and organic moieties. Between 365 and 465 °C, about 9% of the weight loss occurred. If this is considered along with the XRD results (Table I), the weight loss was probably caused by the conversion of Co<sub>3</sub>O<sub>4</sub> to LiCoO<sub>2</sub>. This was followed by a plateau region up to 850 °C and thereafter, a weight loss of about 6% took place up to 1000 °C, caused by lithium evaporation.<sup>20</sup> Figures 2(a) and 2(b) show the XRD lines corresponding to JCPDS data files 82-0330 and 50-0653 for cubic and rhombohedral LiCoO<sub>2</sub>, respectively. Figures 2(c-i)–2(c-iv) show the x-ray diffractograms for the as-synthesized (sample C) and the heat-treated samples (C3, C5 and C8) with the *hkl* values given in parentheses. The diffractogram of sample C [Fig. 2(c-i)] is marked by several broad peaks suggesting a smaller crystallite size and/or poor crystallinity. All the peaks were identified with a cubic spinel phase of LiCoO<sub>2</sub> along with cubic CoO. The peaks at  $2\theta = 42.7$  and  $2\theta = 69.54$ , marked with asterisks [Fig 2(c-i)], are the 100% and 50% peaks of CoO.<sup>22</sup> The diffractogram for sample C3 [Fig. 2(c-ii)] shows the peak with *hkl* (311) at  $2\theta = 37.08$  as the most intense peak, characteristic of cubic LiCoO<sub>2</sub>, and the other notable peaks are those with *hkl* (111) at  $2\theta = 19.08$ , (220) at  $2\theta = 31.42$ , and (440) at  $2\theta = 65.46$ . The peak with *hkl* (531) at  $2\theta = 69.54$  can be seen distinctly in Fig. 2(d-i). Quantitative phase analysis shows the presence of cubic LiCoO<sub>2</sub> (46%) and Co<sub>3</sub>O<sub>4</sub> (54%). The characteristic peaks of Co<sub>3</sub>O<sub>4</sub> are superimposed with those of cubic LiCoO<sub>2</sub> and are shown with square symbols [Fig. 2(c-ii)]. The absence of any CoO in this sample implies that upon heating to 300 °C, the high temperature stable CoO is converted to the low temperature stable form, Co<sub>3</sub>O<sub>4</sub>. The diffractogram for the sample C5 is shown in [Fig. 2(c-iii)]. The peaks show an increase in intensity and sharpness, indicating increased crystallinity. The diffractogram is marked by prominent changes in comparison to Fig. 2(c-ii). The peak at  $2\theta = 37.54$  shows a decrease in intensity, and

the peak at  $2\theta = 19.08$  shows an increase. Also, the (220) peak at  $2\theta = 31.42$  disappears and the peaks at  $2\theta = 65.70$  and  $69.80$  show a splitting [Figs. 2(c-iii) and 2(d-ii)] characteristic of the rhombohedral LiCoO<sub>2</sub>. The phase analysis results indicate the presence of both cubic and rhombohedral phases of LiCoO<sub>2</sub>, the relative proportion being 15% and 85%, respectively. No oxide of cobalt is detected, suggesting complete conversion of Co<sub>3</sub>O<sub>4</sub> to LiCoO<sub>2</sub> on heat-treating at 500 °C. These results are in conformity with the results of thermal analysis as shown in Fig. 1(b).

Figure 2(c-iv) shows the x-ray diffractogram for sample C8. The peaks are very sharp, suggesting a higher degree of crystallinity. All the peaks could be indexed as the rhombohedral phase of LiCoO<sub>2</sub>. The peak (003) at  $2\theta = 19.08$  now is the most intense peak, and the higher

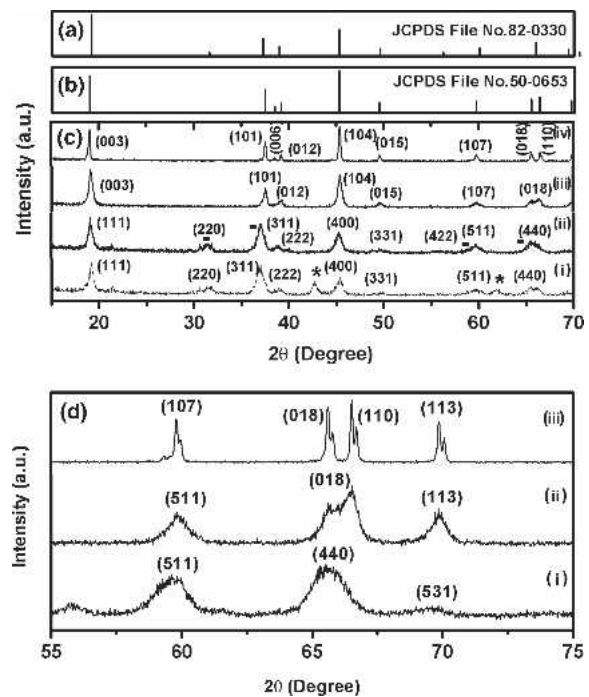


FIG. 2. Standard XRD lines for (a) cubic LiCoO<sub>2</sub> and (b) rhombohedral LiCoO<sub>2</sub>. (c) X-ray diffractograms of LiCoO<sub>2</sub> nanocrystalline powders calcined at different temperatures: (i) as-synthesized, (ii) 300 °C, (iii) 500 °C, and (iv) 800 °C (\* denotes the CoO phase and ■ denotes the Co<sub>3</sub>O<sub>4</sub> phase). (d) Slow-scanned x-ray diffractograms of nanocrystalline LiCoO<sub>2</sub> powders calcined at different temperatures: (i) 300 °C, (ii) 500 °C, and (iii) 800 °C.

angle peaks at  $2\theta = 65.54$  (018) and  $66.46$  (110) are completely split [Figs. 2(c-iv) and 2(d-iii)], which is characteristic of rhombohedral LiCoO<sub>2</sub>. Also, the peak at  $2\theta = 69.82$  shows some splitting [Fig. 2(d-iii)]. The peaks (006) at  $2\theta = 38.53$  and (012) at  $2\theta = 39.19$  [Fig. 2(c-iv)] are well separated in C8 but exhibited an overlapped profile in the reflection patterns of C3, as observed in several other studies as well.<sup>4,8,9,22,23</sup> The prominent changes in the higher angle peaks were revealed by the slow-scanned x-ray diffractograms [Fig. 2(d)] of samples C3, C5, and C8 in the range  $55^\circ \leq 2\theta \leq 75^\circ$ , where the splitting of peaks at  $2\theta = 65.6$ ,  $66.52$ , and  $69.88$  can be clearly observed. A detailed phase analysis along with lattice parameters is summarized in Table I. To complement XRD data for phase determination of rhombohedral and cubic LiCoO<sub>2</sub>, a FTIR study was carried out on sample C3 and C8 in the wave number range  $2500\text{--}400\text{ cm}^{-1}$ , and the results are shown in Fig. 3. The spectra were analyzed in terms of localized vibrations of CoO<sub>6</sub> and LiO<sub>6</sub> moieties in the layered rhombohedral structure of LiCoO<sub>2</sub>. The spectrum of C8 shows characteristic vibrational peaks for rhombohedral LiCoO<sub>2</sub> of space group  $R\bar{3}m$  (C8) in the region of  $600\text{--}400\text{ cm}^{-1}$  corresponding to the rock-salt band, broken into distinct peaks at  $616$  and  $510\text{ cm}^{-1}$  closely resembling values found in the literature.<sup>24–28</sup> These vibrations are due to the stretching of Co–O bonds and bending of O–Co–O bonds in the CoO<sub>6</sub> octahedral moiety of rhom-

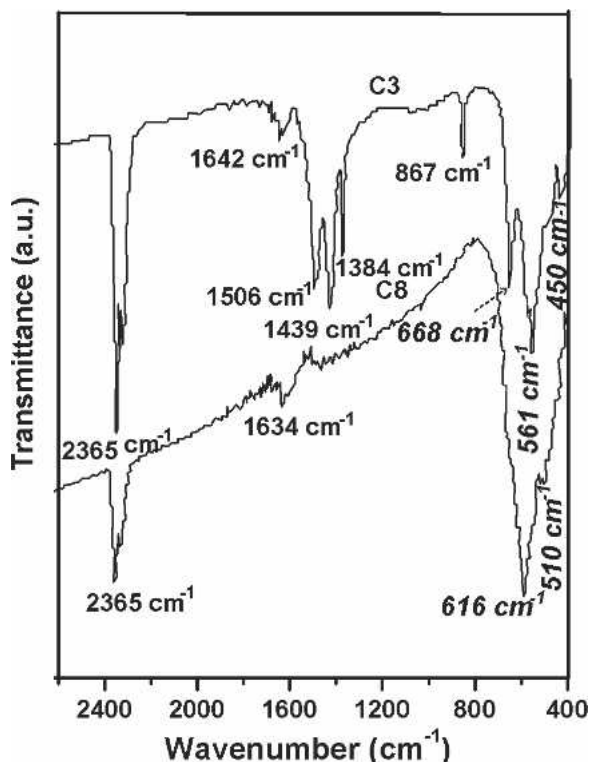


FIG. 3. FTIR spectra of nanocrystalline LiCoO<sub>2</sub> calcined at  $300^\circ\text{C}$  (C3) and at  $800^\circ\text{C}$  (C8).

bohedral LiCoO<sub>2</sub>.<sup>24,25</sup> The vibrations due to the LiO<sub>6</sub> octahedral moiety occur in the region of  $200\text{ cm}^{-1}$  and therefore could not be recorded due to instrumental limitations. The FTIR spectrum for the sample C3 was found to be different from that of rhombohedral LiCoO<sub>2</sub> (C8), showing the characteristic broad bands. It shows peaks at  $450$ ,  $561$ ,  $668\text{ cm}^{-1}$  with a small shoulder at  $867\text{ cm}^{-1}$ . The broad peaks found in the region of  $1650\text{--}1200\text{ cm}^{-1}$  are due to residual organic moieties like the nitrate and carboxylate group. The sharp peak in the region of  $2365\text{ cm}^{-1}$  found for both the samples (C3 and C8) is due to ambient CO<sub>2</sub>. Appearance of more modes in the spectrum of C3 than those for C8 indicates a distortion in the rhombohedral structure and suggests a cubic spinel type of structure.<sup>25</sup> A small band in the region of  $\sim 450\text{ cm}^{-1}$  may be assigned to the disordered structure of the precursor in C3, which is completely absent in C8 with formation of a more ordered layered structure.<sup>25</sup>

Field emission scanning electron (FE-SEM) micrographs for both cubic (C3) and rhombohedral LiCoO<sub>2</sub> (C8) powders show an agglomerated nature of the particles (Fig. 4). The estimated powder grain sizes are  $\sim 60\text{ nm}$  for the cubic and  $\sim 100\text{ nm}$  for the rhombohedral phase. However, the respective crystallite sizes, as

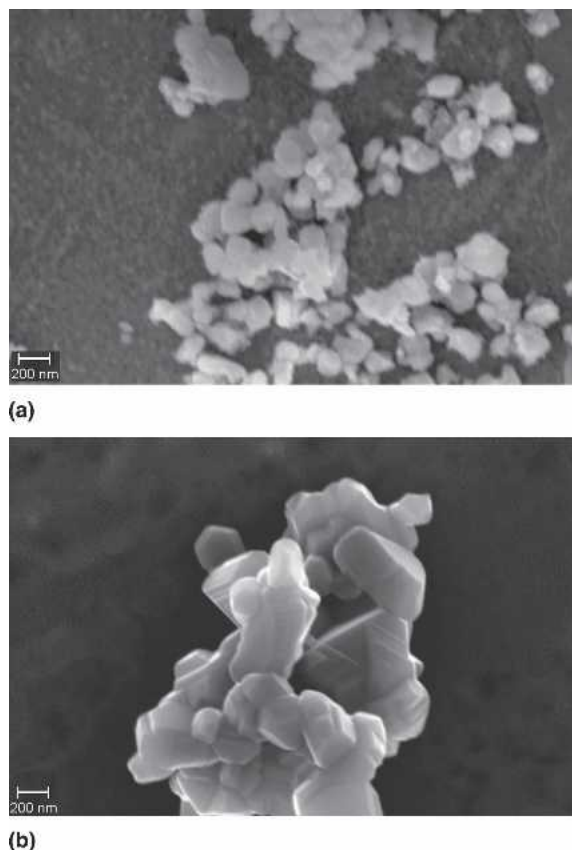


FIG. 4. FE-SEM micrographs of LiCoO<sub>2</sub> samples: (a) C3, calcined at  $300^\circ\text{C}$  and (b) C8, calcined at  $800^\circ\text{C}$ .

determined by XRD size analysis from the peak broadening, are found to be ~10 nm and ~51 nm (Table I).

Figure 5 shows the optical absorption spectra for samples C3, C5, and C8. The spectrum for Co<sub>3</sub>O<sub>4</sub> is also included in the figure for comparison. The band gap values for the LiCoO<sub>2</sub> phase were estimated from the differential plot,  $\delta A$  versus wavelength, shown for sample C8 as a representative plot in the inset in Fig. 5. All the spectra are marked by three regions of absorption: I and II in the lower energy and III at the band edge. The spectra for both C3 and Co<sub>3</sub>O<sub>4</sub> are very similar, and the estimated band gaps are ~1.43 and 1.47 eV, respectively. Two prominent shoulders are observed for all the samples in the lower energy region at ~0.65 and ~0.88 eV, similar to the observation of Kushida et al.,<sup>5</sup> originating probably due to some defect levels or from the electronic structure near the bottom of the conduction band. It is possible that some Co<sup>2+</sup> ions on the tetrahedral sites might be responsible for this. It is interesting to note that although the cation distribution is different in the case of cubic LiCoO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub>,<sup>15</sup> there is a striking similarity between the optical spectra of sample C3 and Co<sub>3</sub>O<sub>4</sub>. With increase in the calcination temperature, the optical spectrum shows remarkable changes, and there is a notable blue shift in the band gap of LiCoO<sub>2</sub> calcined at 800 °C.<sup>5</sup> The band gap was found to be ~1.7 eV with shoulders of ~0.8 and ~0.65 eV. Variation in lithium

content in the samples may strongly influence the band structure of LiCoO<sub>2</sub>; however, from the ICP analyses the Li:Co ratio was found to be 1.02 for all the samples. Therefore, the observed blue shift in the band gap of C8 is not due to the variation in stoichiometry. As shown by XRD analysis, the phase present is 100% rhombohedral LiCoO<sub>2</sub>, of space group  $R\bar{3}m$ . The octahedral ligand field of oxygen ions is strong enough to cause spin pairing in Co<sup>3+</sup> ions to form a lower valence band comprising of completely filled  $t_{2g}$  orbitals and a conduction band of two empty  $e_g$  orbitals, and the d-d transition of electrons takes place between these two levels of Co.<sup>5,14</sup> As the crystallite size in the rhombohedral phase was found to be higher than that in the cubic phase (Table I), the observed blue shift cannot be explained on the basis of the size effect and must be related to changes in the electronic structure. On passing from higher symmetry (cubic) to lower symmetry (rhombohedral), the valence band now is composed of three completely filled  $t_{2g}$  orbitals and the conduction band is formed from two empty  $e_g$  orbitals of low spin Co in the octahedral ligand field of oxygen ions. Here, the splitting between the  $t_{2g}$  and  $e_g$  orbitals increases by a factor of 9/4 of that in the tetrahedral field of Co in the cubic lattice of LiCoO<sub>2</sub>.<sup>16</sup> The band gap of ~1.7 eV found for sample C8 agrees well with the calculated band gap value of rhombohedral LiCoO<sub>2</sub> by Czyzyk et al.<sup>14</sup> Thus, the band gap of rhombohedral LiCoO<sub>2</sub> is about 0.3 eV higher than the cubic form.

The open circuit voltage (OCV) of a lithium ion cell can be given by the relation<sup>29</sup>

$$V_{OC} = (\phi_C - \phi_A)/e_0 \quad (1)$$

where  $\phi_C$  and  $\phi_A$  are the cathode and anode work functions respectively, and  $e_0$  is the magnitude of an electric charge. As  $\phi_C$  becomes larger,  $V_{OC}$  increases. The electronic band structure of the cathode has a large influence on the work function of the cathode. The band gap in LiCoO<sub>2</sub> is formed by the separation between the  $t_{2g}$  non-bonding levels and the  $e_g$  antibonding levels that are again formed by the  $\pi$ -overlap between  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals and oxygen 2p orbitals and by the  $\sigma$ -overlap between  $d_{3z^2-r^2}$  and  $d_{x^2-y^2}$  orbitals and oxygen 2p orbitals, respectively.<sup>30</sup> Both theoretical<sup>13,14,16</sup> and experimental works suggest that in cobalt oxide, the Fermi level resides within the  $t_{2g}$  band while in LiCoO<sub>2</sub>, it is above the  $t_{2g}$  band, close to it. As Li is intercalated into the oxide, the electron is transferred to the  $t_{2g}$  levels lowering the Fermi energy and increasing the work function of the cathode, resulting in an increase in the intercalation voltage and increased OCV. Indeed, it has been observed experimentally that the electrochemical extraction of Li takes place at a constant voltage plateau at 3.6 V on open circuit for Li/cubic LiCoO<sub>2</sub> cell,<sup>8</sup> whereas for Li/rhombohedral Li<sub>x</sub>CoO<sub>2</sub> cell, the open circuit voltage is 4.5 V for  $x = 1.0$ .<sup>31</sup>

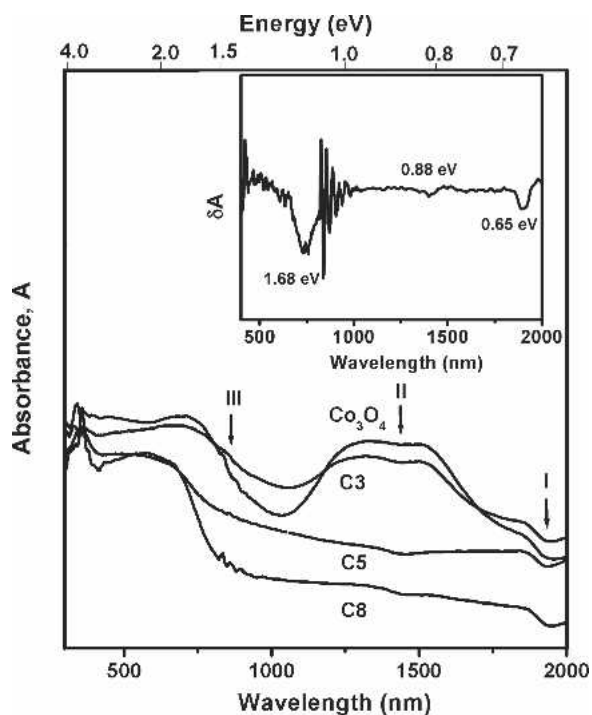


FIG. 5. UV-vis absorption spectra for nanocrystalline LiCoO<sub>2</sub> powders calcined at different temperatures at 300 °C (C3), 500 °C (C5), and 800 °C (C8). The spectrum for Co<sub>3</sub>O<sub>4</sub> is also shown for comparison. The inset shows a differential absorbance plot ( $\delta A$ ) versus wavelength for sample C8.

In contrast to the present results, Kushida et al.<sup>5</sup> observed a large red shift (0.9 eV) in the band gap of HT-LiCoO<sub>2</sub> for thin films deposited on SiO<sub>2</sub> substrates. However, thin films have always been known to have a band gap higher than that of bulk material.

The optical spectra of C5 lie in the region intermediate to the spectra of C3 and C8 with a band gap similar to C8 (~1.7 eV). The investigated band gap suggests a rhombohedral crystal structure for the sample C5, which is further supported by the quantitative x-ray analysis in Table I that shows a dominant rhombohedral phase along with a minor cubic phase of LiCoO<sub>2</sub>. An additional transition at energies greater than 3.3 eV is also observed for all the samples and may be attributed to Li 1s to O 2p or O 2p to Co 3d transitions.

#### IV. CONCLUSIONS

Nanocrystalline (10–50 nm) LiCoO<sub>2</sub> powder can be obtained by combustion synthesis. As-synthesized powder has a cubic crystal structure, which gradually transforms irreversibly into the rhombohedral form at temperatures greater than 500 °C. A drastic change in the *d-d* transition is observed between these two structural forms of LiCoO<sub>2</sub>. The transition becomes sharper and the band gap is blue-shifted by about 0.3 eV when the material passes from the higher to the lower symmetry. These findings partly explain why the electrochemical performance of rhombohedral LiCoO<sub>2</sub> is better than that of the cubic form.

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