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# $LiCoO_2$ CERAMICS POWDERS DOPED WITH EUROPIUM

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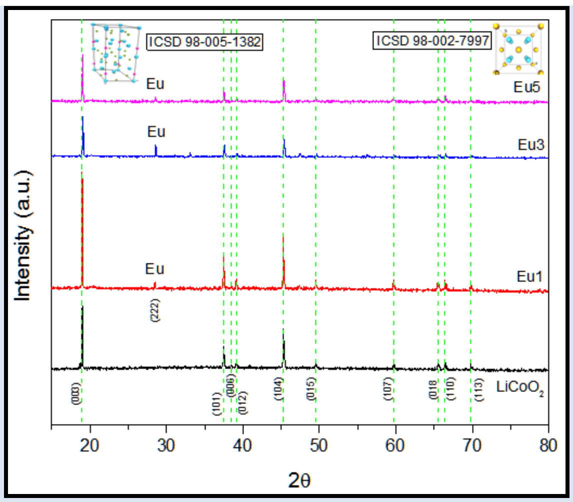


## ABSTRACT

Lithium cobaltate ($LiCoO_2$) is one of the materials used to make cathodes for lithium-ion batteries. However, it is subject to various limitations, such as structural and thermal instability, low electrochemical capacity, irreversibility, and insecurity. Newer materials are designed and produced with rare earths a low concentration, to promote the better electrochemical performance of lithium-ion batteries. The europium ion ($Eu^{3+}$) has advantageous properties, such as an ionic radius that is larger than the radii of lithium and cobalt, and thermomechanical and structural stability. In this paper, is reported on the production of crystalline lithium cobaltate ($LiCoO_2$) powders doped with $Eu^{3+}$ at different concentrations (0.01, 0.03, and 0.05 mol %). There are various methods for producing these powders, such as the solid-state, hydrothermal, and sol gel methods, among others. However, the sol-gel method makes it possible to obtain crystalline materials at low residence temperatures, to control variables during synthesis, and to produce materials of high purity at nanometric sizes. The materials obtained were analyzed by various characterization techniques such as, IR spectroscopy (FTIR), x-ray diffraction (XDR), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM) to determine the morphological and compositional properties after doping with $Eu^{3+}$. Structural analysis and Rietveld refinement showed a hexagonal structure at 800 °C, with planes attributable to the R-3m space group. By means of FTIR, bands characteristic of $LiCoO_2$ and the band corresponding to $Eu^{3+}$ were observed. When the $Eu^{3+}$ ion was added at different concentrations, the morphology of the particles was uniform and quasispherical. The elements were identified by EDS as cobalt and europium. Through TEM, the interplanar distance of the main plane of $LiCoO_2$ doped with $Eu^{3+}$ were obtained, that is, (003) and an increase in the plane took place when the $Eu^{3+}$ was incorporated ion into the crystalline structure.

***Keywords:*** sol-gel, lanthanide, europium, nanoparticles, lithium-cobalt, powders.

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## POLVOS CERÁMICOS DE $LiCoO_2$ DOPADOS CON EUROPIO


### RESUMEN

El cobaltato de litio ($LiCoO_2$) es uno de los materiales utilizados en las baterías de ion-litio como cátodo. Sin embargo, ha presentado diversas limitaciones como: inestabilidad estructural y térmica, baja capacidad electroquímica, irreversibilidad e inseguridad. La producción de nuevos materiales está diseñando con tierras raras en bajas concentraciones, para promover un mejor rendimiento electroquímico de las baterías de ion-litio. Debido a las propiedades del ion europio ($Eu^{3+}$) como el radio iónico que es más grande comparado con el del litio y cobalto, estabilidad termomecánica y estructural. En este artículo, se reporta la producción de polvos cristalinos de cobaltato de litio ($LiCoO_2$) dopados con $Eu^{3+}$ a diferentes concentraciones (0.01, 0.03 y 0.05 % mol). Para la producción de los polvos de $LiCoO_2$ dopados con $Eu^{3+}$ existen diversos métodos como: estado sólido, hidrotermal, sol gel, entre otros. Sin embargo, el método sol-gel permite la obtención de materiales cristalinos a bajas temperaturas de residencia, un control de las variables durante la síntesis, materiales altamente puros y de tamaños nanométricos. Los materiales obtenidos fueron analizados por diversas técnicas de caracterización como: espectroscopia Infrarroja (IR),, difracción de rayos x (DRX), microscopia electrónica de barrido (MEB), espectroscopia dispersiva de energía (EDS) y microscopia electrónica de transmisión (MET) para analizar las propiedades morfológicas y composicionales después de dopar con $Eu^{3+}$. El análisis estructural y el refinamiento Rietveld mostraron una estructura hexagonal a 800 °C con planos atribuidos al grupo espacial R-3m. Por medio de FT-IR, se observaron bandas características del $LiCoO_2$ y la banda correspondiente al $Eu^{3+}$. La morfología de las partículas fueron uniformes y quasiesféricas cuando se agregó el ion $Eu^{3+}$ a diferentes concentraciones. Finalmente, los elementos fueron identificados por EDS como cobalto y europio. Por MET se obtuvieron las distancias interplanares de los planos principales de $LiCoO_2$ dopado con $Eu^{3+}$, es decir, (003) y un aumento del plano al incorporar el ion $Eu^{3+}$ en la estructura cristalina.


***Palabras Claves:*** sol-gel, lantánidos, europio, nanopartículas, litio-cobalto, polvos.

## 1. INTRODUCTION

Lithium cobaltate ($LiCoO_2$) is a layered material with a rhombohedral structure with a space group R-3m. It has two structural phases, a high-temperature (HT-$LiCoO_2$) and a low-temperature (LT-$LiCoO_2$) phase and is commonly used in the production of cathodes for lithium-ion batteries. According to Tan et al. [1] $LiCoO_2$ is reversible, that is, it can generate the deintercalation and intercalation of lithium ions during charging and discharging respectively, with an operating voltage of 4.2 V and a capacity theoretical 274 $mAhg^{-1}$. In lithium-ion battery cathodes, it has various applications, as in electric vehicles or portable devices; however, it has an experimental capacity well below the theoretical capacity, as Zeng et al. y Wright et al. [2], [3] point out, and become irreversible, promoting structural and thermal changes that limit its use in high-energy systems. Given the limitations presented by current materials, new technologies are being developed to obtain cathode materials doped with transition metals; for instance, Sivaraj et al. [4] proposed the substitution of trivalent rare-earth ions to improve electrochemical performance, causing a defect in the network by partial replacement. Furthermore, these strategies are aimed at improving structural stability, electronic conductivity, and discharge capacity. Rare-earth elements comprise 17 elements of the periodic table: scandium and yttrium and a group of elements called lanthanides (La-Lu). According to Zhao et al. [5] these elements have been used in low concentrations as doping agents. Tamura et al. [6], Wu et al. [7], and Yanwen et al. [8] report that lanthanides are of great interest as doping agents because of their thermomechanical stability and their ionic radius, which is greater than those of cobalt (0.63 Å) and lithium (0.60 Å). Specifically, europium has an ionic radius of 1.12Å, which can cause an increase in the lattice parameter, leading to a greater ease of Li transport and, causing a deformation in the crystal lattice, according to Ning et al. [9]. In addition, incorporating the europium ion in the lithium cobaltate structure provides ionic, chemical, and mechanical stability. It is well-known that properties of materials depend on the use of appropriate synthesis method. The choice of the sol-gel method was due to advantages that it offers, such as, chemical purity, low residence times and greater control of experimental variables. Rahim et al. [10] mentions that it prevents unwanted impurities and makes it possible to obtain fine particles. Also, with the sol-gel method, different precursors can be used, such as alkoxides, nitrates, sulfates, and oxides, among others. However, alkoxides are more expensive than the other precursors. For this reason, nitrates were selected to produce $Eu^{3+}$-doped $LiCoO_2$ crystalline materials. The cost of the synthesis in terms of electrical and thermal expense are lower compared to other synthesis methods, such as the solid-state method, where the residence temperatures are >1000 °C. In the synthesis by the sol-gel method, the europium nitrate content was used in low quantities, however, the method can produce large quantities of products for application in lithium-ion batteries.

## 2. EXPERIMENTAL PROCEDURE

Different europium doped $LiCoO_2$ systems were obtained at different mol % concentrations (0.01, 0.03 and 0.05) with a stoichiometric ratio of [1:1] for the transition metal and the alkali metal. Lithium nitrate ($LiNO_3$), cobalt nitrate hexahydrate $(CoNO_3)_2*6H_2O$, europium (III) nitrate hexahydrate $(EuNO_3)_3*5H_2O$ and citric acid ($C_6H_8O_7$) (Sigma Aldrich 99 %) were used as precursor sources. Initially, the metal salt was prepared with precursors to form homogeneous colloidal particles under constant agitation. Subsequently, the synthesis temperature was increased to 60 °C for 30 min to obtain a homogeneous solution, and the doping agent for each matrix was added after 30 min under constant stirring. Then, chelating agent (citric acid) was added to the precursors at a stoichiometric ratio of [1:2], and the temperature was increased to 80 °C to accelerate the reaction and obtain a wet gel. Finally, the wet gel was heated at 130 °C for 24 h to remove the remaining agents, followed by a heat treatment at 800 °C for 24 h which yielded a crystalline ceramic material as seen in Figure 1.

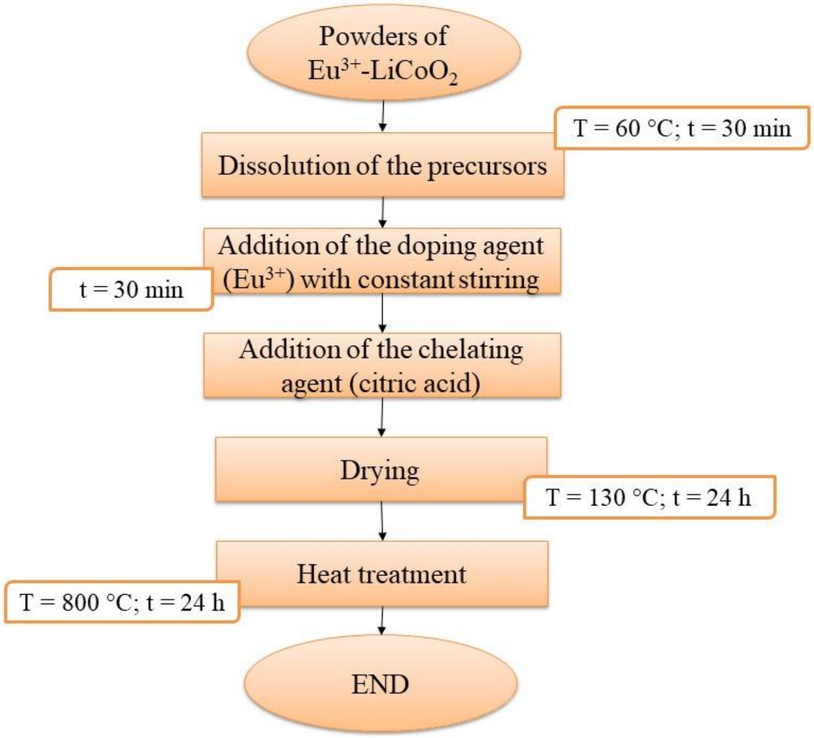


**Figure 1.** Method for producing the $Eu^{3+}$-doped $LiCoO_2$ powders.

The powders obtained by the sol-gel route were characterized by various analytical techniques to evaluate their structural, chemical, morphological, and compositional properties. Fourier transform infrared spectroscopy (FT-IR) to used KBr pellets was performed with a Perkin Elmer Spectrum 65 Spectrometer to analyze the powders and identify the characteristic vibrational absorption bands of $LiCoO_2$ treated with a $Eu^{3+}$ doping agent. X-ray diffraction (XDR) with a Bruker Eco D8 ADVANCE diffractometer was used to determine the crystalline structure. The XRD pattern of the powder was recorded using CuKa1 radiation (1.5418 Å) with a fraction angle range of 15° to 80°, (0.02 s steps). The Bragg reflections of the prepared material and the influence of the dopant in the structure were established by Rietveld refinement. The morphological characteristics of the samples were examined with scanning electron microscope (SEM), using a HITACHI TM3030 microscope at 15 kV, with graphite tape and a charge reduction (NL), to avoid excessive charging of the particles. In addition, a high-resolution analysis was done with JSM 6701F-6701 microscope. Finally, a semi-quantitative chemical analysis of the elements was performed by energy dispersed x-ray spectroscopy 7 (EDS) at resolutions of 3,000x and 25,000x, and transmission electron microscopy (TEM) with a JEM-2100 microscope.

## 3. RESULTS AND DISCUSSION

### Compositional Analysis: Fourier Transform Infrared Spectroscopy.

Once the powders were obtained with heat treatment at 800 °C, the samples were prepared as KBr pellets to be analyzed by (FT-IR). Figure 2 shows the spectra of the powders obtained from $LiCoO_2$ doped with europium at 0.01 (Eu1), 0.03 (Eu3) and 0.05 (Eu5) mol %.

Frequency bands were found at approximately 528 $cm^{-1}$ [11] corresponding to the Li-O bond, with a stretching vibration at approximately 1390 $cm^{-1}$, which can be attributed to the carbonyl group with the lithium and cobalt metal ions [12].

Finally, the europium bond, shown as M-O at 598 $cm^{-1}$ [13], correlates with the lack of an O-Co-O bond, due to the large ionic radius of europium, which has the benefit of binding with oxygen and reducing the presence of cobalt (Co-O), which results in HT-$LiCoO_2$ (high temperature $LiCoO_2$).

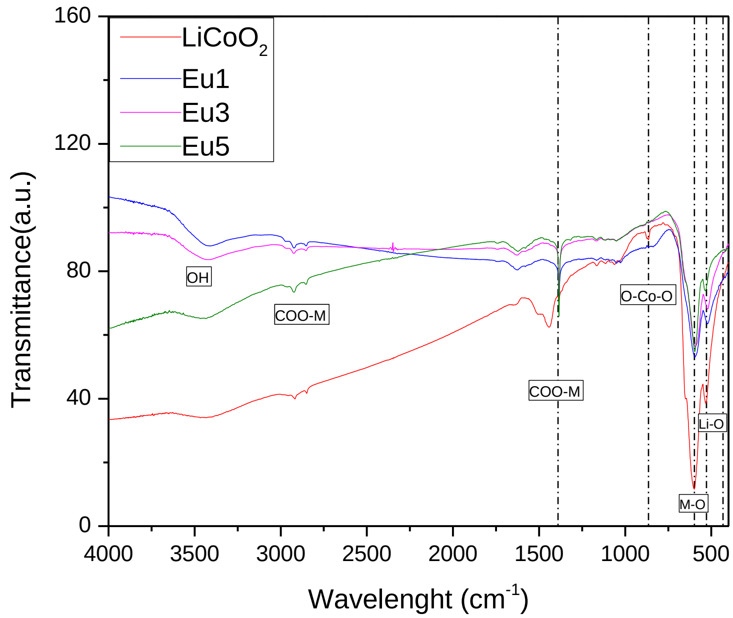


**Figure 2.** Spectra of $LiCoO_2$ ceramic powders doped with europium at 0.01, 0.03, and 0.05 mol %, with heat treatment at 800 °C.

## Structural Analysis: X-Ray Diffraction

Figure 3 shows the XRD patterns of the powders heat-treated at 800 °C, they exhibit a hexagonal crystalline structure corresponding a stratified layer with the space group R-3m [14]. Two peaks of greater intensity are observed at approximately 18° and 45°, which correspond to the (003) and (104) planes, respectively, and which can be attributed to the layered oxide materials. In addition, there are two double peaks associated with a high degree of crystallinity, corresponding to planes (006) and (012), at 38° and 39°, respectively [15], and to planes (018) and (110), found at 65° and 66° [16], respectively. In addition, in the doped samples, a small diffraction peak attributable to the $Eu^{3+}$ ion is seen at approximately 29° corresponding to the (222) crystal plane. The presence of the $Eu^{3+}$ ion within the crystalline structure of $LiCoO_2$ caused a shifting of the planes to the right, due to the ionic radius of the europium ion, which is larger than those of cobalt and lithium. To calculate the average size of the crystallite, the Scherrer equation was used, as seen in Figure 4. The values in the equation are as follows: K is the Scherrer constant, $\lambda$ is the wavelength of the light rays used, is the full width at half-maximum of the peak (,i.e., the FWHM), and is the Bragg angle. The calculated values for pure $LiCoO_2$ and $LiCoO_2$ doped with $Eu^{3+}$ at 0.01, 0.03, and 0.05 mol % are shown in Table 1; due to the incorporation of the europium ion in the structure, there was an increase in the size of the crystallite. Rietveld refinement values of 1.89, 1.81, 1.94, and 1.82 were obtained for $LiCoO_2$, doped with $Eu^{3+}$ at 0.01, 0.03, and 0.05 mol %, respectively: these values represent the R factor (R= (I(006)+I(012)/I(101)), indicating a hexagonal ordering. On the other hand, the ratios of the values of the lattice I(003)/I(104) were 0.8414 for the $LiCoO_2$ sample, 1.03 for the sample doped with 0.01 mol %, 1.25 for the sample doped with 0.03 mol %, and 1.009 for the one doped at 0.05 mol %. According to the literature, the ratio of the (003)/(104) peaks indicates the presence of a mixture of cations in the layered structure.

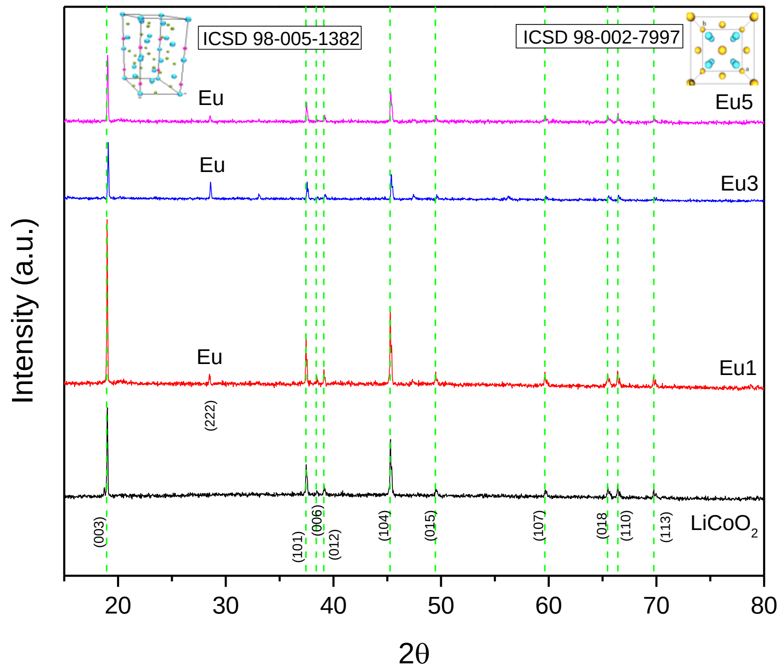


**Figure 3.** Diffractograms of the $LiCoO_2$ ceramic powders doped with europium at 0.01, 0.03, and 0.05 mol %, with heat treatment at 800 °C.

$$D = \frac{K\lambda}{\beta\cos\theta}$$

**Figure 4.** Scherrer equation for calculating the average crystallite size.

**Table 1.** Average crystallite sizes calculated by means of the Scherrer equation.

| Samples | Crystallite size (nm) |
|---|---|
| $LiCoO_2$ | 12.89 |
| $LiCoO_2$:Eu1 | 18.60 |
| $LiCoO_2$:Eu3 | 26.07 |
| $LiCoO_2$:Eu5 | 23.04 |

For cathodic materials suitable for electrochemical tests, the desired values are > 1.2 [17]. The 0.03 mol % sample presents a low mixture of cations (Li and Co), therefore, the sample doped at 0.03 mol % possesses the properties required for cathodes in lithium-ion batteries. Table 2 shows the Rietveld refinement data for $LiCoO_2$ and the doped powders. The values of the structural parameters of the lattice of the non-doped powders differ from those of the doped powders, confirming the distortion of the structure and the displacement of the peaks due to the presence of the doping agent (europium ions) [16], [18]. Also, the values of goodness of fit (GOF) are lower than 2. Nageswara et al. [19] report that the c/a ratio corresponds to the structure stability possessed by the $LiCoO_2$ layered structure. The theoretical value of the c/a ratio is 4.899, and the calculated values for the synthesized samples ($LiCoO_2$:Eu1, $LiCoO_2$:Eu3, and $LiCoO_2$:Eu5) are higher than that (4.992, 4.991, 4.991, and 4.993, respectively), which indicated that the samples have excellent structural stability.

**Table 2.** Rietveld refinement values: lattice parameters of the samples obtained by the sol-gel method.

| Samples | a | c | c/a | I(003)/I(104) | R | GOF | d-spacing plane (003) $LiCoO_2$ |
|---|---|---|---|---|---|---|---|
| $LiCoO_2$ | 2.8154 | 14.0547 | 4.992 | 0.843 | 1.893 | 0.868 | 4.640 |
| $LiCoO_2$:Eu1 | 2.8156 | 14.0551 | 4.991 | 1.032 | 1.813 | 0.989 | 4.672 |
| $LiCoO_2$:Eu3 | 2.8159 | 14.0568 | 4.991 | 1.257 | 1.946 | 1.130 | 4.648 |
| $LiCoO_2$:Eu5 | 2.8161 | 14.0609 | 4.993 | 1.009 | 1.829 | 0.841 | 4.661 |

### Morphological Analysis: Scanning Electron Microscopy (SEM)

The results from the morphological analysis of the $LiCoO_2$ powders with a thermal treatment of 800 °C are reported in Figure 5, at two powers of magnifications (3,000x and 25,000x). The micrographs showed irregular morphologies with micrometric sizes. According to the Jing et al. [20] two factors that characterize an excellent material for use in cathodes are the size and morphology of the particles. At nanometric sizes, there is a greater surface area between the electrolyte and the active material ($LiCoO_2$), which promotes a greater electrochemical response.

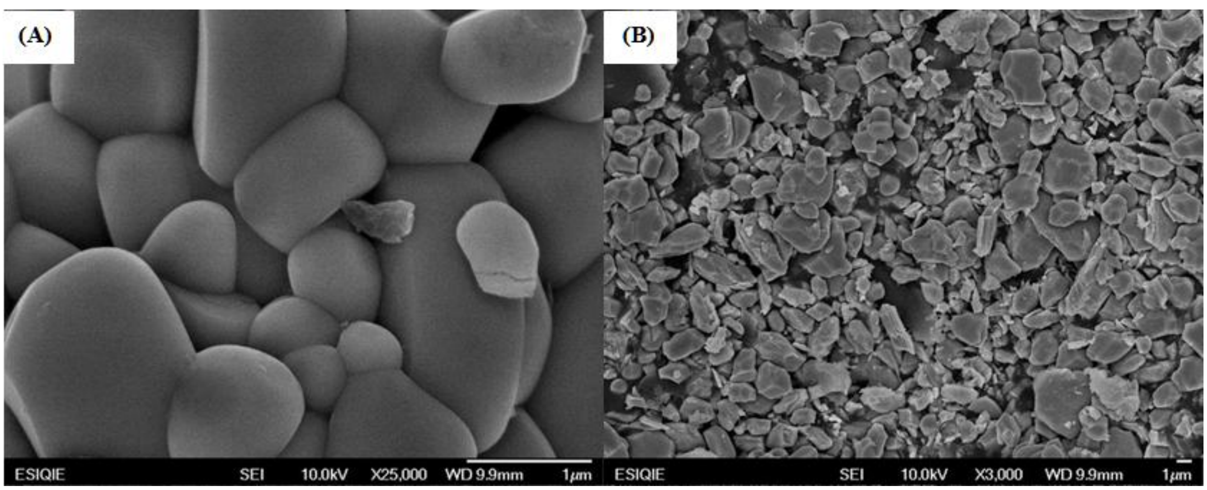


**Figure 5.** High resolution micrograph of the $LiCoO_2$ ceramic powders, with heat treatment at 800 °C at magnifications of 3,000x (A) and 25,000x (B).

Micrographs of the $LiCoO_2$ powders doped with $Eu^{3+}$ at 0.01, 0.03, and 0.05 mol % are shown in Figure 6. The morphology of the particles became quasiesferical and uniform in the presence of the $Eu^{3+}$ ion at the different molar concentrations. According to the Guofeng et al. [21], "Smooth surfaces and clear boundaries indicate the crystallinity of the powders."

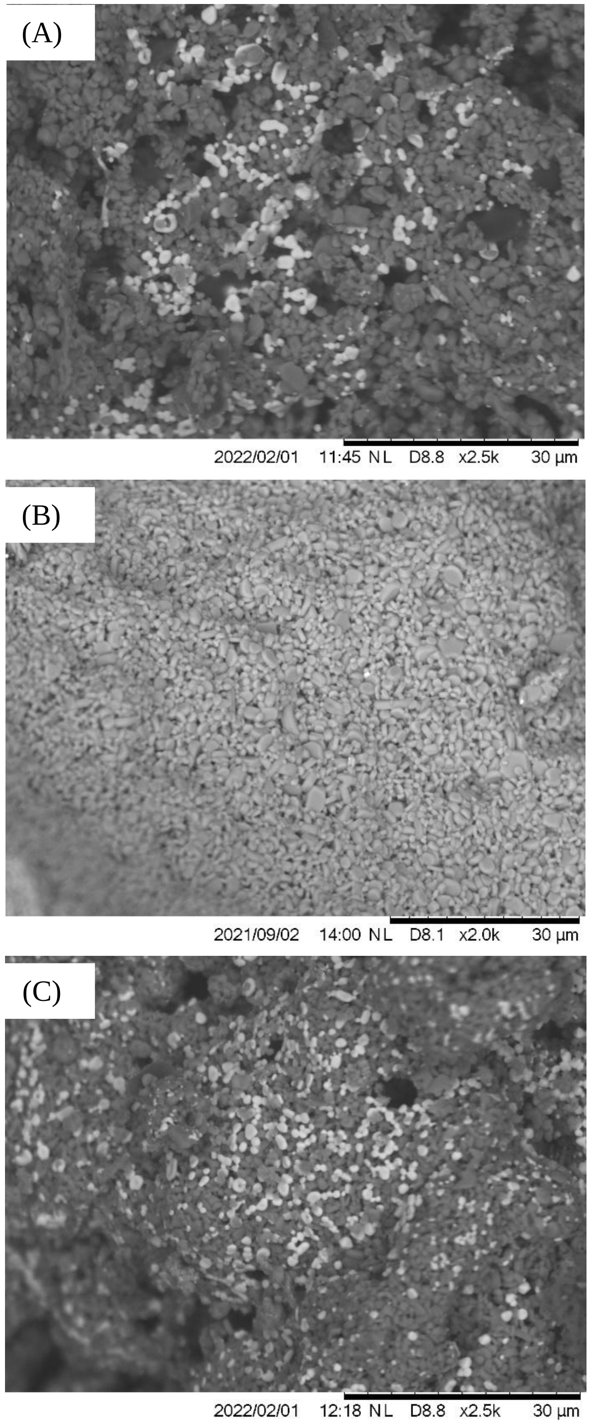


**Figure 6.** High resolution micrograph of ceramic powders of the $LiCoO_2$ doped with europium at 0.01 (A), 0.03 (B), and 0.05 (C) mol %, with heat treatment at 800 °C.

### Elemental Chemical Analysis: Energy Dispersive Spectroscopy (EDS)

Upon examination by energy dispersion spectroscopy (EDS), peaks associated with the presence of cobalt, carbon, and oxygen were observed, as can be seen in Figure 7. Lithium was not observed because it has a very low energy value and is not detectable. The mapping of the sample indicates the presence of cobalt in blue and of oxygen in red. According to the Xiabo et al. [22], it can be observed that “the elements are distributed on the surface of the particles.” In addition, there are a few peaks, such as peaks for gold (Au) and palladium (Pd), which were part of the holder. Furthermore, Table 3 shows the values for oxygen and cobalt as regards weight % and atomic %.

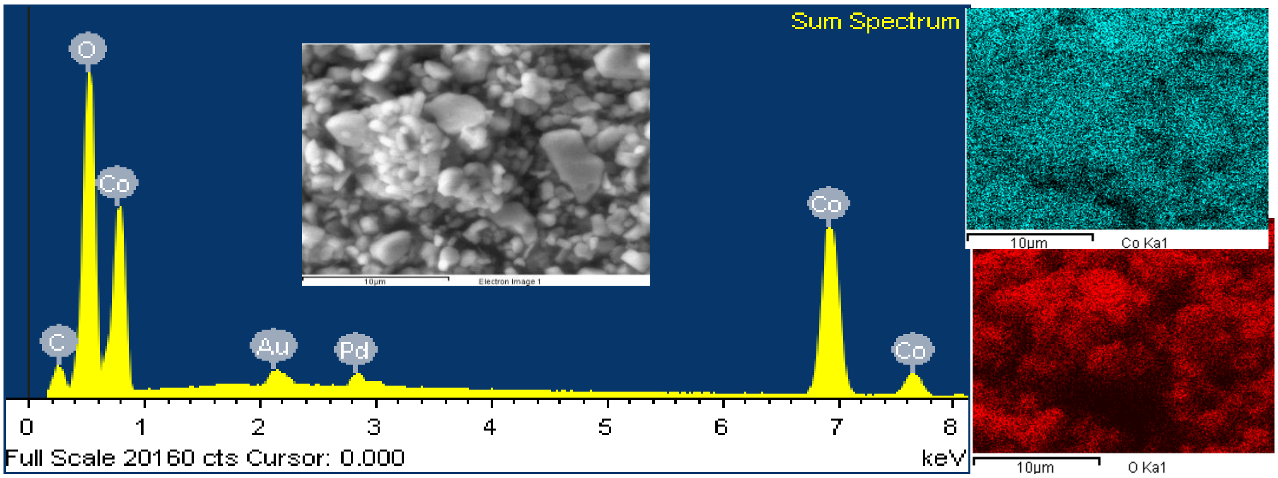


**Figure 7.**Semiquantitative analyses of the elements present in the $LiCoO_2$ ceramic powders, with heat treatment at 800 °C.

**Table 3.** Values (weight % and atomic %) of the elements present in the samples, obtained by EDS on the $LiCoO_2$ sample.

| Element | Weight% | Atomic% |
|---|---|---|
| Oxygen | 30.99 | 62.33 |
| Cobalt | 69.01 | 37.67 |
| Total | 100 | |

In the europium-doped samples presented in Figures 8-10, cobalt, oxygen, and europium were found. These caused the amount of cobalt to decrease, at 0.05 mol % more dopant (17.59 %) and less cobalt (37.11 %) were obtained. Examined by means of EDS, the main elements obtained were attributed to the HT-$LiCoO_2$ powders and to the presence of the europium at different concentrations.

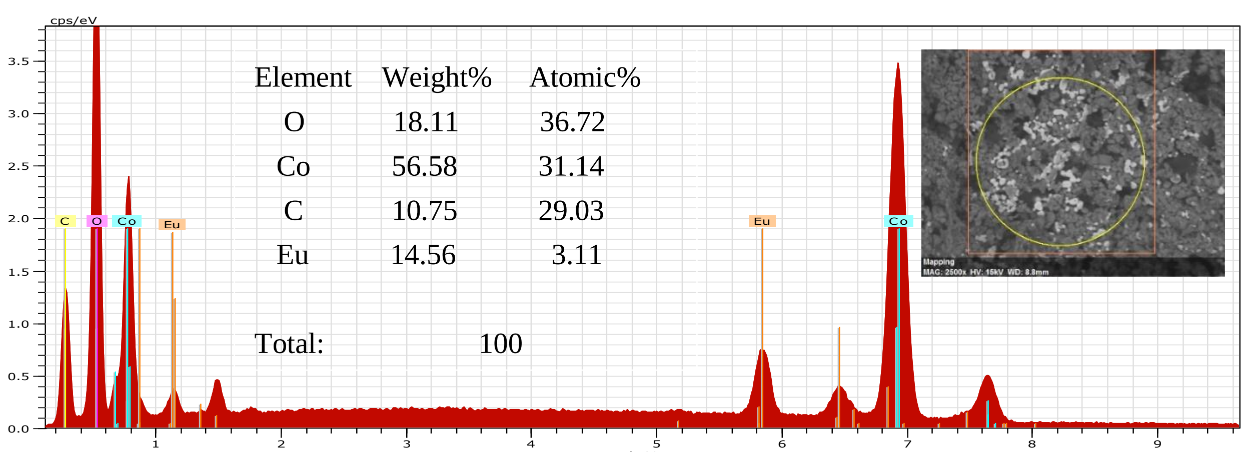


**Figure 8.** Semiquantitative analysis of the elements present in the $LiCoO_2$ ceramic powders doped with $Eu^{3+}$ at a 0.01 mol %, with heat treatment at 800 °C.

Cobalt weight % of the sample doped with europium at 0.01, 0.03, and 0.05 mol % decreased when the europium ion is present in the structure.

The carbon possibly came from the graphite tape used for SEM analysis.

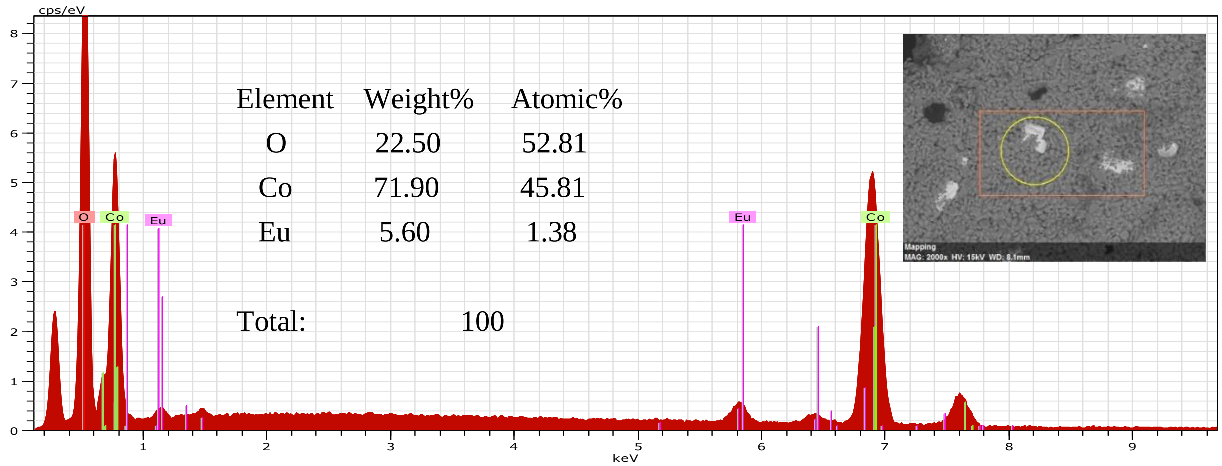


**Figure 9.** Semiquantitative analysis of the elements present in the $LiCoO_2$ ceramic powders doped with europium at a concentration of 0.03 mol %, with heat treatment at 800 °C.

At higher concentrations of the europium ion (0.03 and 0.05 mol %), the weight % cobalt decreases. Therefore, the higher the europium concentration, the lower the cobalt content, due to the partial replacement of cobalt ions by europium that form the structure.

The carbon possibly came from the graphite tape used for SEM analysis.

Oxygen was generated due to sample handling or ambient conditions.

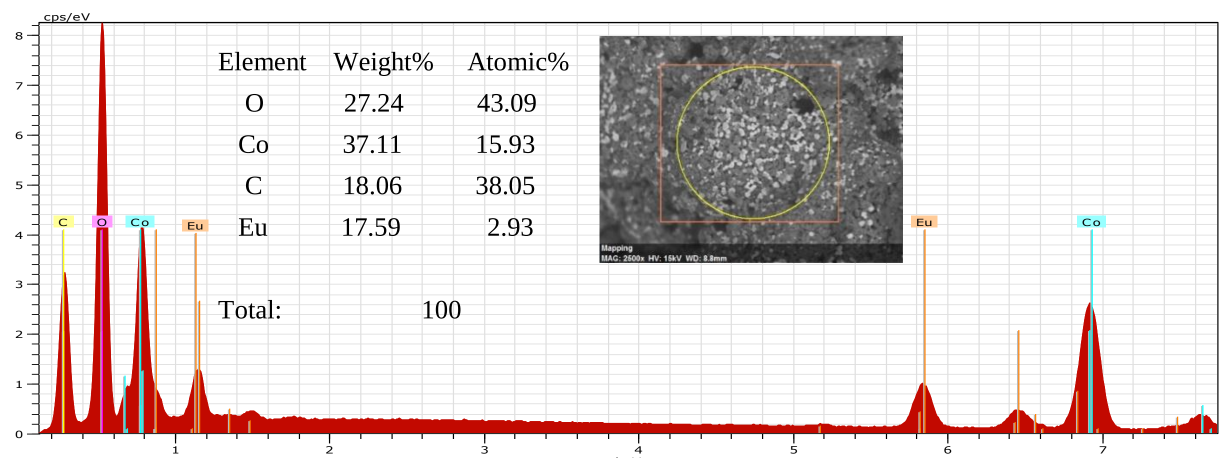


**Figure 10.** Semiquantitative analysis of the elements present in the $LiCoO_2$ ceramic powders doped with europium at a concentration of 0.05 mol %, with heat treatment at 800 °C.

## Morphological Analysis: Transmission Electron Microscopy (TEM)

The powders obtained from the $LiCoO_2$ doped with $Eu^{3+}$ at 0.01, 0.03, and 0.05 mol % were analyzed by transmission electron microscopy. Interplanar distances were determined using Digital Micrograph software with selected area electron diffraction (SAED) analysis.

The values of the planes found by TEM were correlated with the values obtained by x-ray diffraction with the Rietveld refinement. Figure 11 shows the results of the SAED analysis of the $LiCoO_2$ powders doped with $Eu^{3+}$ at 0.01 mol %. The interplanar distance obtained was 4.683 nm, which corresponds to the (003) plane of $LiCoO_2$ fits with to the d-spacing value of the Rietveld refinement obtained from the diffractograms.

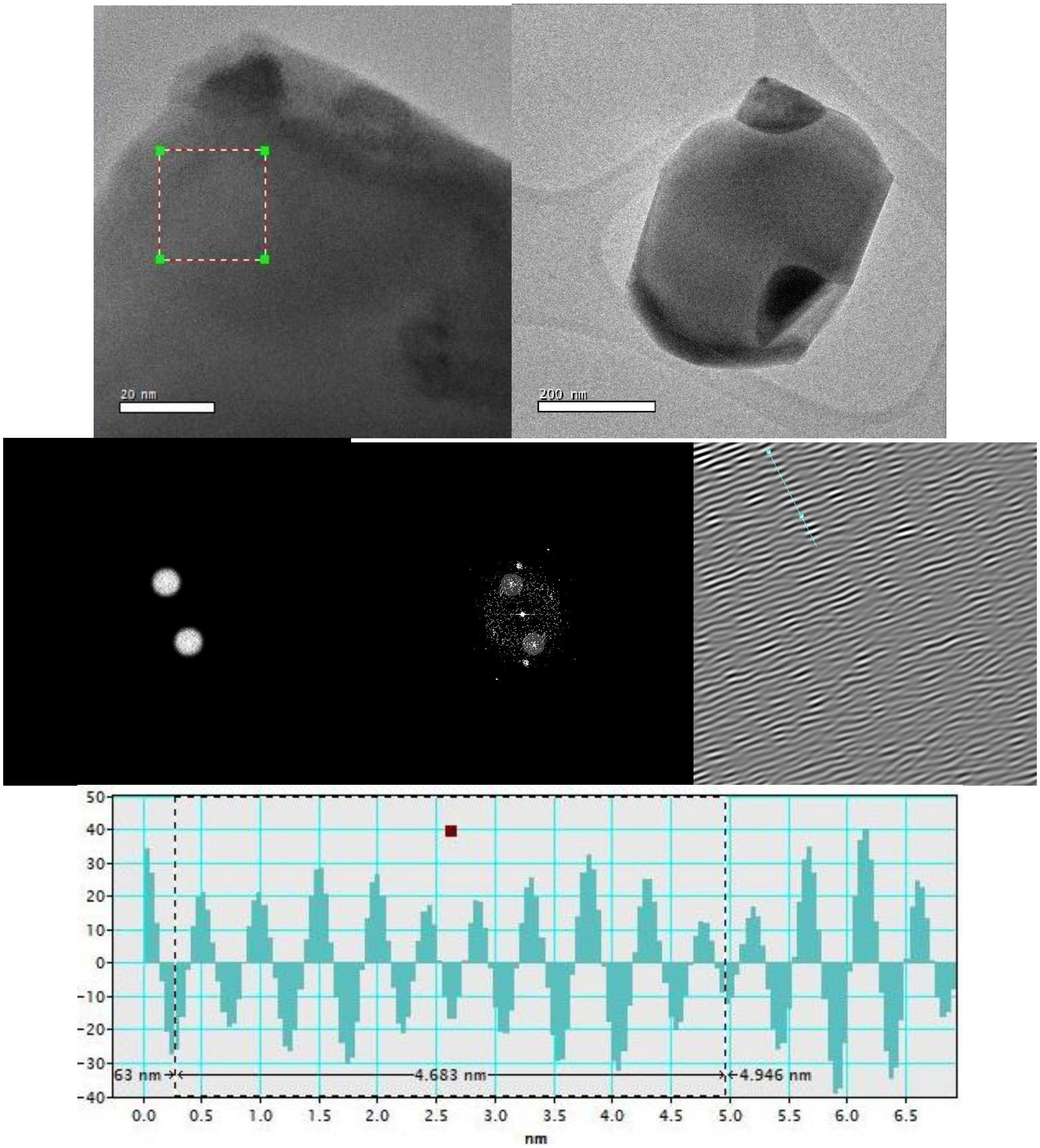


**Figure 11.** TEM micrographs of the $LiCoO_2$ powders doped with $Eu^{3+}$ at 0.01 mol %, with the SAED analysis.

Figure 12 shows the results of the SAES analysis of the $LiCoO_2$ powders doped with $Eu^{3+}$ at 0.03 mol %. The interplanar distance obtained was 4.653 nm, which corresponds to the (003) plane of $LiCoO_2$

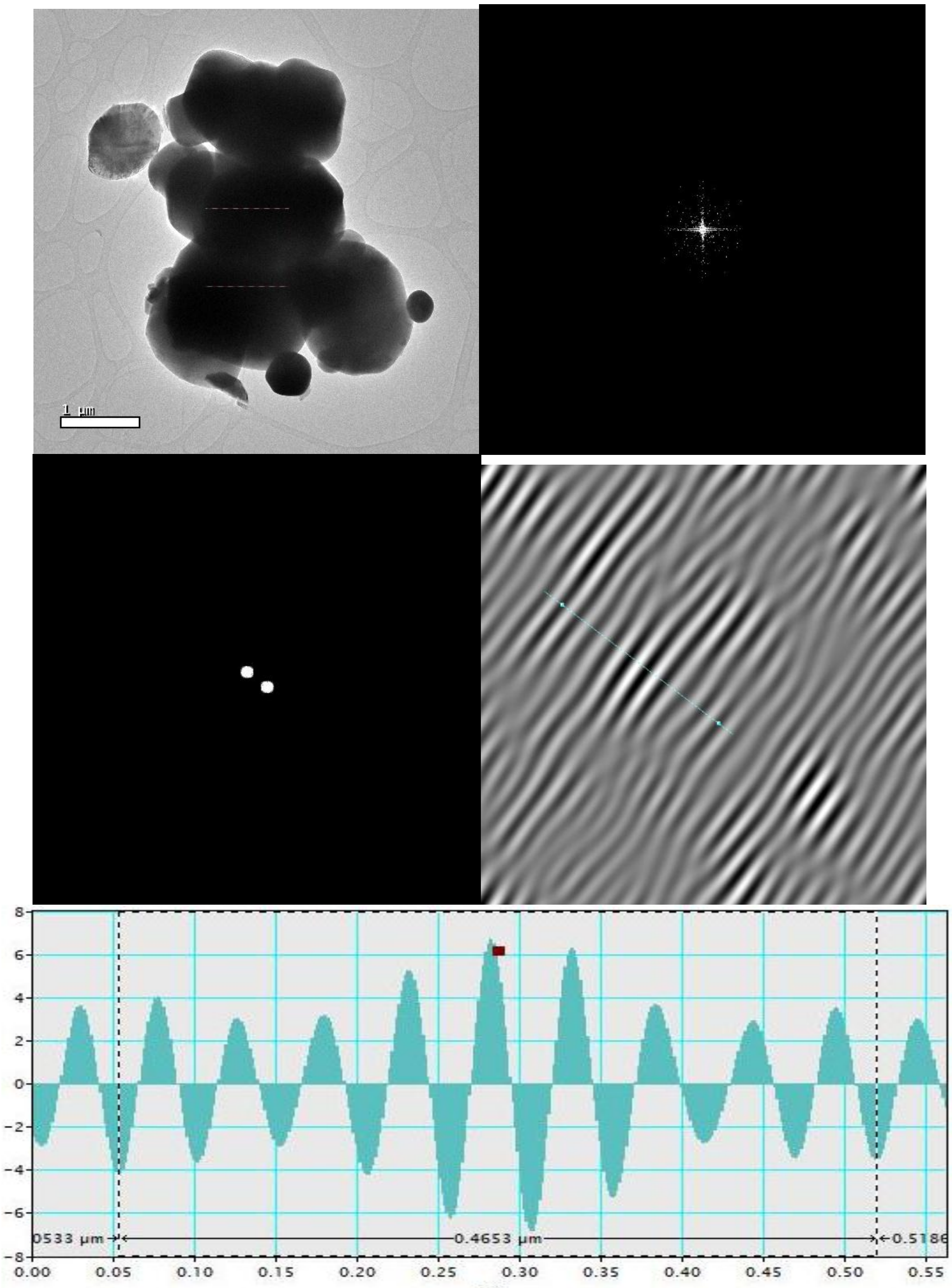


**Figure 12.** TEM micrographs of the $LiCoO_2$ powders doped with $Eu^{3+}$ at 0.03 mol % with SAED analysis.

In Figure 13, the results of the SAED analysis of the $LiCoO_2$ powders doped with $Eu^{3+}$ at 0.05 mol % are reported. The interplanar distance of the (003) plane was 4,749 nm. The interplanar distance of all the samples are matches with to the d-spacing in the Rietveld refinement analysis.

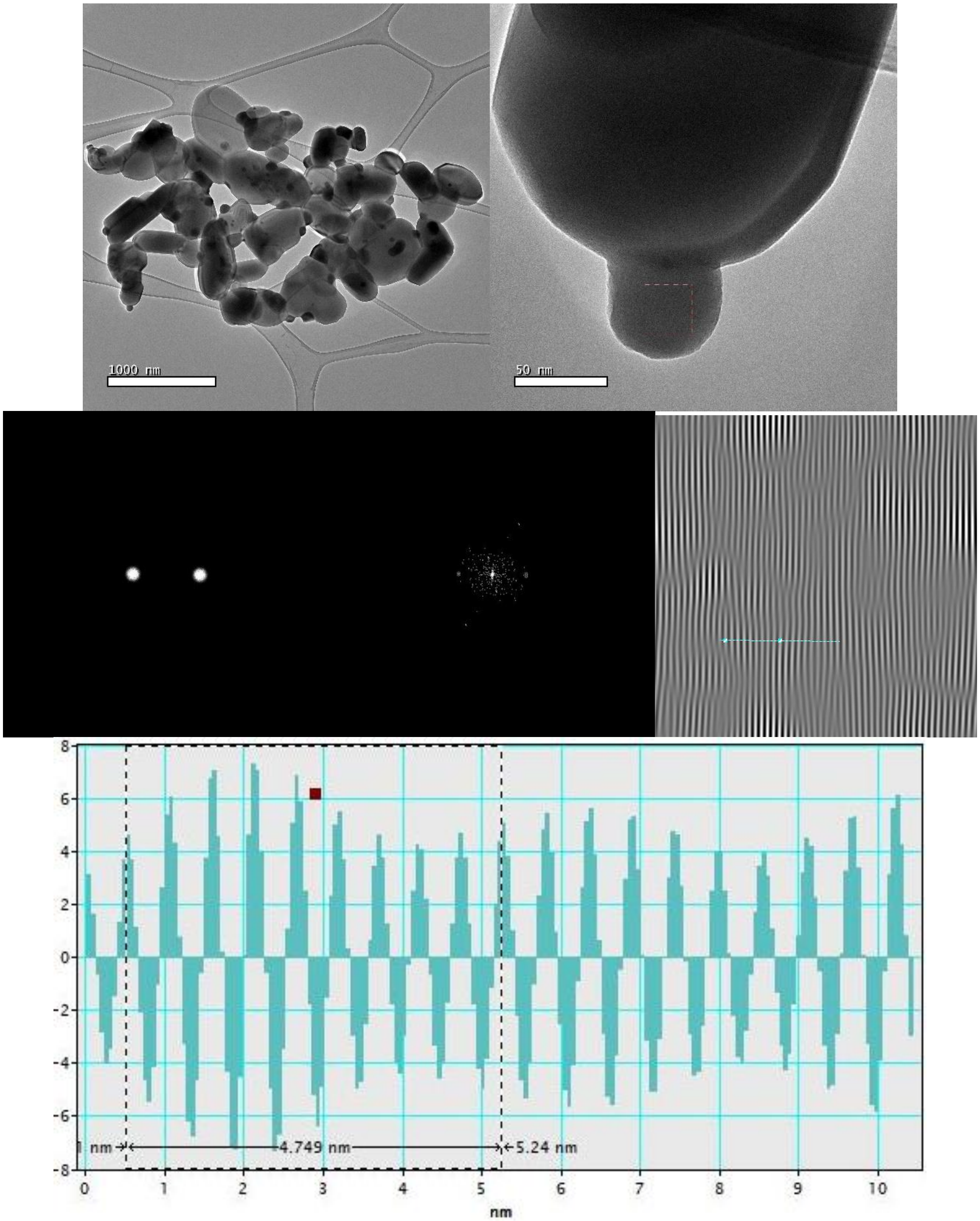


**Figure 13.** TEM micrographs of the LiCoO2 powders doped with $Eu^{3+}$ at 0.05 mol % with SAED analysis.

The distance from the (003) plane of pure $LiCoO_2$ increased when it was doped with $Eu^{3+}$ at the different concentrations. According to Colín et al. [23], this behavior is caused by the presence of the $Eu^{3+}$ ion in the crystal structure.

## 4. CONCLUSION

The results of this study show that the use of the sol-gel route with a chelating agent was a satisfactory method for obtaining ceramic powders of HT-$LiCoO_2$ doped with europium at different molar concentrations. All the powders studied exhibited a hexagonal structure at a temperature of 800 °C. Judging from the goodness-of-fit values and the intensity of the (003)/(104) peaks, the outstanding sample was the one europium-doped at 0.03 mol %, which had peaks intensity values above 1.2.

These results reflect an increase in cell volume due to the ionic radius of europium. In addition, although the incorporation of europium did not modify the morphology of the particles since the chelating agent facilitated the formation of crystallites but not the union of the species or the growth of the grains. Elemental chemical analysis confirmed the composition of the material. However, a small amount of carbon and oxygen were present. The results obtained by TEM showed a correlation with the results obtained by XRD, that is, the interplanar distance of the (003) plane coincided with the d-spacing identified by the Rietveld analysis. According to the results of this study, $LiCoO_2$ materials doped with europium at various concentrations show promise for future electrochemical evaluations provided their synthesis is carefully managed so as not to generate impurities in the materials. On the other hand, it is suggested to pay attention to the modification of the pH to study the behavior of the reaction kinetics and the morphology of nanoparticles. The materials obtained in this research have a potential use in cathodes in lithium-ion batteries, because, in the industry, the material of choice since the 1990's has been $LiCoO_2$, but its electrochemical performance is limited by several factors. However, the incorporation of rare-earth ions makes it possible to produce lithium-ion batteries with better electrochemical performance and better thermal and structural stability. In this study, the most promising sample was $LiCoO_2$ doped with $Eu^{3+}$ at 0.03 mol %.

## 5. ACKNOWLEDGMENT

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