

## A VERSATILE METHOD TO OBTAIN NANO STRUCTURES OF CoSe FROM AQUEOUS SOLUTION

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This paper presents a new method for obtaining cobalt selenide. Corresponding studies were conducted to obtain UV bands prohibited direct and indirect energy for this compound, which values are in 1.74 eV and 0.22 eV, in addition, there is a peak at 275 nm showing a high absorption in the ultraviolet region. HRTEM studies were performed to elucidate the crystal structure of the compound, finding characteristic values of 3.4 Å and 4.4 Å for an orthorhombic structure and stoichiometry of Co<sub>9</sub>Se<sub>8</sub>. FTIR confirms the existence of Co<sub>9</sub>Se<sub>8</sub> nanoparticles and the study is complemented by RAMAN acquiring characteristic peaks for the synthesized compound. Finally, a study was conducted by XPS gaining characteristic peaks corresponding to CoSe.

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### 1. Introduction

The research community has focused on the design of rational methods to synthesize the formation of controllable nanoparticle chalcogenides. This synthesis has been done using traditional methods or by developing new techniques which usually demand high temperatures, high pressures, toxic precursors, and special matrices[1] with specific sizes, morphologies, and structures with potential applications in electronics, biochemical sensors, and catalysis, just to name a few[2]. Recently, Co-based chalcogenide has been a new research topic mainly because of its low cost [3] and the six-electron system of valence orbitals of the selenium<sup>[4]</sup>. Selenium atoms are combined with metals to form binary chalcogenide compounds with several properties such as a semiconductor to metallic transition, valence transition and structural phase transition. These compounds are having numerous applications in modern technology such as switching devices, electrical and optical phase change data storage technologies, photo conductors, photo

electrochemical energy conversion electrode, flexible radiometry and IR-imaging bundles for endoscopy, and sensitive detector for high field magnetic resonance imaging applications [5-13]. In this work, we describe a method to obtain CoSe based on an ionic exchange where selenium powder is mixed with a rongalite solution and ammonium hydroxide for posteriorly react it with cobalt chloride, this method was reported by Castillo et al.[14]

## 2. Experimental details

Selenium ions were synthesized by preparing a solution based on four reagents such as 2 ml of rongalite 1M, 2 ml of deionized water, 2 ml of ammonium hydroxide 2M, and 30 mg of selenide. A heating plate temperature was used to heat the solution until reaching a crystalline appearance, then 30 mg of cobalt chloride ( $\text{CoCl}_2$ ) were added to the solution and stirred vigorously at 25 °C. This process resulted in the formation of dark precipitates to obtain cobalt selenide compound samples. Finally, these samples were washed with by centrifugation pure water and dried in a desiccator for 24 hours.

Subsequently, the composition of cobalt selenide samples were analyzed. An UV-vis spectrum was performed on the samples using a UV-vis lambda 2 spectrophotometer. The chemical composition of the samples were studied through the XPS Perkin-Elmer Phi-5000. The morphology and the energy dispersive spectroscopy (EDS) of the samples were investigated by high resolution transmission electron microscopy (HRTEM) using a JEOL 5400LV. For the Raman spectroscopy, a Horiba Jobin Yvon Spectrometer MicroRaman with a source laser excitation and detector of 1024 pixels with high sensitivity CCD was use. The MicroRaman was mounted on an Olympus microscope BX41TF with spatial resolution  $<1 \mu\text{m}$ . The lasers used had three excitation ranges of 532 nm, 638 nm and 785 nm with spectral resolutions of  $1.8 \text{ cm}^{-1} / \text{pixel}$  (532nm) and  $1.1 \text{ cm}^{-1} / \text{pixel}$  (785 nm). In this study, the power increments of the lasers were 100%, 50%, 25%, 10%, 1% and 0.1%. Lastly, the laser beam was focus using a 50x objective over a 2 micron surface of the sample; the Raman scattered beam was captured with the same objective. While the FTIR was done in a Nicolet Protege 460 equipment.

## 3. Results

A room temperature UV-Visible absorption measurement was made to cobalt selenide (Fig. 1). Optical absorption spectra indicate a direct and indirect band gap of 1.74 eV and 0.22 eV respectively, the optimal band energy gap is 1.4 eV for a cell made of a single material [15]. Maneepprakorn et al.[16], has reported a direct band gap of 1.45 eV. Furthermore, it exists a peak in 275 nm showing high absorption in the ultraviolet region which makes it a candidate as UV filter. This band gap was determined using the absorption spectrum and Tauc's Model<sup>[17]</sup> that is given to:

$$\alpha h\nu = A(h\nu - E_g)^n$$

where  $\alpha$  is the absorption coefficient,  $h$  is the Planck's constant,  $\nu$  is the frequency,  $A$  is a constant,  $E_g$  is the energy band gap and to obtain the direct band gap  $n = 1/2$  and  $n = 2$  for indirect band gap. The value of direct and indirect band gap was obtained by extrapolating linear portion of the curve  $(\alpha h\nu)^2 = 0$  and  $(\alpha h\nu)^{1/2} = 0$  respectively.

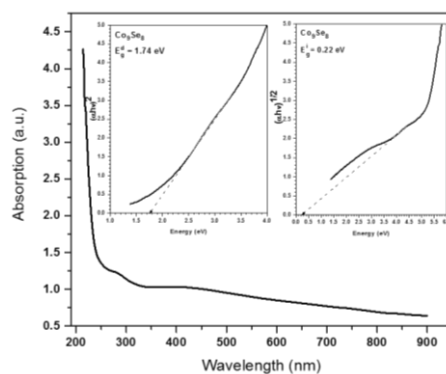


Fig. 1. Absorption response of the  $\text{Co}_9\text{Se}_8$  compound, left inset corresponds to the direct bandgap of 1.74 eV and right inset corresponds to indirect bandgap of 0.22 eV.

HRTEM micrographs shown in Fig. 2 through a scale indicated of 5nm the existence of nanocrystals where can be observed corresponding lines with interplanar spacings. In Figure 2 (a) the inset shows the Fourier transform of the contrast image which is the main and the image (b) that is at the right of the figure, corresponds to the inverse Fourier transform where the full processing where is observed a grid with spacings of 3.14 Å and 4.4 Å. From this information we identified the material through stoichiometry  $\text{Co}_9\text{Se}_8$  Corresponding to powder diffraction files (PDF) 09-0233 and 65-3116. Miller indices according to one of the spacings are (3 1 1), the other interplanar distance has not been identified and this is attributable to the presence of residual elements in the synthesis.

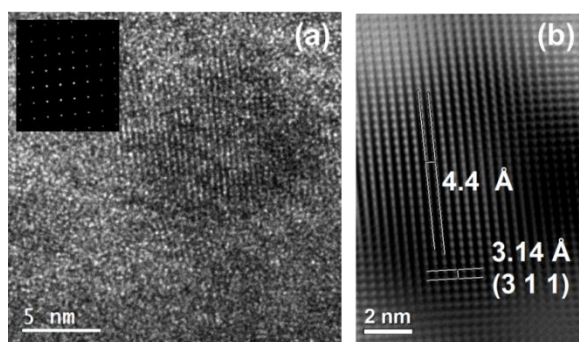


Fig. 2. Micrographs of  $\text{Co}_9\text{Se}_8$  compounds, where to the left shown a representative contrast image and to the right a higher magnification.

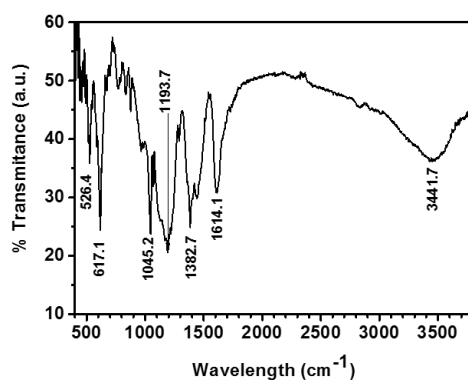


Fig. 3. FTIR absorption spectra to  $\text{Co}_9\text{Se}_8$  show peaks characteristic that correspond to the formation of nanoparticles of cobalt selenide

FTIR spectrum show bands in  $3441.7$  and  $1614.1$   $\text{cm}^{-1}$  for O-H stretching and metal oxygen bonding, This is also due to the possible absorption of  $\text{H}_2\text{O}$  in the sample. Indeed, water absorption is very common in this powder especially when exposed to the environment, so it can be concluded that the sample is free of the solvents used for part where the cobalt selenide. Studies by Markova[18] and Aripionammal[4], show that the band at  $526.4$   $\text{cm}^{-1}$ , this band correspond to links Co-O indicating the formation of cobalt oxide and the vibrations of the Co-Se bonding is in  $671.1$   $\text{cm}^{-1}$ , this intense peak is reason to complete the formation of nanoparticles of cobalt selenide, furthermore, in  $1045.2$  and  $1382.7$   $\text{cm}^{-1}$  cobalt complex exist with corresponding O-H in plane bending and O-H stretching, this information is shown in Fig. 3.

The Raman spectrum is shown in Figure 4, corresponding to  $192$   $\text{cm}^{-1}$  peak specifically corresponds to CoSe, this has been reported by Zhu et al. [19], and we can also conclude that the compound is rich in selenium because bridges Co-Se[13], on the other hand, the bands at  $475$  and  $626$   $\text{cm}^{-1}$  are related to cobalt oxide, which are also reported by Osswalda et al. [20] and Campos et al. [21]. The weak Raman Peak in  $993$   $\text{cm}^{-1}$  can be associated to the Orthorhombic CoSe phase.

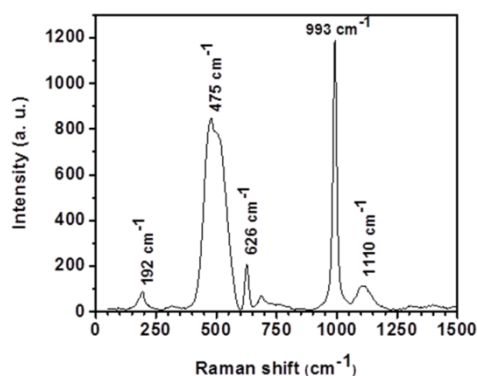


Fig. 4. Raman show peaks obtained for the  $\text{Co}_9\text{Se}_8$  compounds, there are five frequencies values also by references

It was also performed a XPS study for this sample, it has been founded energy links, characteristic of cobalt and selenium. The representative peaks of Co  $2p_1$  and  $2p_3$  Co are shown at  $802$  eV and  $782$  eV, while the Selenium peaks are at  $163$  eV and  $57$  eV, for  $3p_3$  and  $3d_5$ . Fig. 5 display the XPS spectrum of the sample related to cobalt selenide. These particular peaks have been reported by Mandale et al. [22] and Zhao et al. [23]

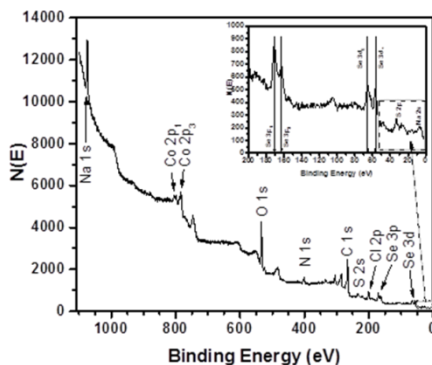


Fig. 5. XPS survey for  $\text{Co}_8\text{Se}_9$  compound, the inset show the selenium presence.

#### 4. Conclusions

This new method of obtaining cobalt selenide has a great advantage compared to traditional methods of obtaining this compound, which occupy more elaborate or techniques procedures and sophisticated equipment. In this paper was clearly observed that the material obtained has the characteristics and properties obtained by other authors, it is important to note that the direct bandgap makes a material capable of attenuating ultraviolet radiation. On the other hand, studies with the above techniques confirm the existence of cobalt selenide formation of very small amounts of trace materials where it began. It notes that the obtained compound has a crystal structure orthorhombic in which a characteristic peak is also located in Raman spectroscopy.

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#### References

- [1] R. Seoudi, et al., *Materials Letters* **61**, 3451 (2007).
- [2] L. Cheng-Cheng, et al, *Applied Catalysis B: Environmental* **119–120**, 139 (2012).
- [3] C. E. M. Campos, et al., *Solid State Communications* **131**, 265 (2004).
- [4] S. Ariponnammal, *Res. J. Recent. Sci.* **3**, 332 (2014).
- [5] X. Li, et al., *Phys Chem. Chem. Phys.* **17**, 800 (2015).
- [6] J. R. McKone, et al., *Energy Environ. Sci.* **4**, 3573 (2011).
- [7] Kenney, M. J. et al., *Science* **342**, 836 (2013).
- [8] S. Hu, et al., *Science* **344**, 1005 (2014).
- [9] J. Ran, et al., *ACS Appl. Mater. Interfaces*, **6**, 17679 (2014).
- [10] E. J. Popczun, et al, *Angew. Chem. Int. Ed.* **53**, 5427 (2014).
- [11] Z. Huang, et al., *ACS Appl. Mater. Interfaces*, **6**, 10408 (2014).
- [12] Y. Li, et al., *J. Am. Chem. Soc.* **133**, 7296 (2011).
- [13] Q. Ding, et al., *J. Am. Chem. Soc.* **136**, 8504 (2014).
- [14] M. Sotelo-Lerma, R. A. Zingaro, S. J. Castillo, *Journal of Organometallic Chemistry* **623**, 81 (2001).
- [15] I. Konovalov, *Thin solid films* **451-452**, 413 (2004).
- [16] W. Maneeprakorn, M. Malik, P. O'Brien, *Journal of Materials Chemistry* **20**, 2329 (2010).
- [17] M. Lakshmi, K. Bindu, S. Bini, K.P. Vijayakumar, C. Sudha Kartha, T. Abe, Y. Kashiwaba, *Thin Solid Films* **386**, 127 (2001).
- [18] Deneva I. Markova, *Journal of the University of Chemical Technology and Metallurgy* **45**, 351 (2010).
- [19] L. Zhu, M. Teo, P.C. Wong, K. C. Wong, I. Narita, F. Ernst, K. A. R. Mitchell, S. A. Campbell, *Applied Catalysis A: General* **386**, 157 (2010).
- [20] C. E. M. Camposa, J. C. de Lima, T. A. Grandia, K. D. Machado, V. Dragoa, P. S. Pizanib, *Solid State Communications*. **131**, 265 (2004).
- [21] A. B. Mandale, S. Badrinarayanan, S. K. Date, A. P. B. Sinha, *Journal of Electron Spectroscopy and Related Phenomena*. **33**, 61 (1984),
- [22] Ü. Alver, E. Bacaksiz, E. Yanmaz, *Journal of Alloys and Compounds*. **456**, 6 (2008).
- [23] D. Zhao, S. Zhang, G. Yin, C. Du, Z. Wang, J. Wei, *Electrochimica Acta* **91**, 179 (2013).