COPPER-SELENIDE AND COPPER-TELLURIDE COMPOSITES POWDERS SINTETIZED BY IONIC EXCHANGE

O. ARELLANO-TÁNORI^{a,b}, M. C. ACOSTA-ENRÍQUEZ^{a*}, R. OCHOA-LANDÍN[°], R. IÑIGUEZ-PALOMARES[°], T. MENDÍVIL-REYNOSO^{c,d}, M. FLORES-ACOSTA^a, S. J. CASTILLO^a

^aDepartamento de Investigación en Física, Universidad de Sonora, Apdo. Postal 5-088, CP. 83000, Hermosillo, Sonora, México.

^bInstituto Tecnológico y de Estudios Superiores de Monterrey, Campus Sonora Norte, Blvd. Enrique Mazón López No. 965, C.P. 83000, Hermosillo, Son., México ^cDepartamento de Física, Universidad de Sonora, Apdo. Postal 1626, CP. 83000 Hermosillo, Sonora, México.

^dCentro de Investigación en Materiales Avanzados, Miguel de Cervantes 120, Complejo Industrial. CP 31109 Chihuahua, Chih., México.

At this research it is provide two precursor solutions of selenium ions (Q') and tellurium ions (Q) used to success easy ways in order to synthetize composites containing mainly the one copper-selenide (CuSe) and the another copper-telluride (CuTe). By Raman spectroscopy the binary copper selenides chemical composition was detected, while from X-Ray photoelectrons spectroscopy (XPS) were observed the binding energies of Se 3d and Cu $2p^3$ of 53 eV and 953 eV, respectively. The Copper selenide morphology was investigated by TEM observing particles are aggregated. Also, the absorption spectrum of copper selenide corresponds to direct band gap of 2.79 eV and indirect band gap of 1.36 eV. In the same way, Raman spectroscopy of chemical composition of teineite was detected for CuTe formulation, similarly XPS expose the Te 3d region shows that the valence of Te is -2, while the Cu 3p region show valence for the copper of +1. Also, TEM images presents a nanocaterpillar and the diffraction pattern corresponding indicates orthorhombic structures for both samples (CuSe and CuTe). Finally, the absorption spectrum for copper telluride indicates a direct band gap of 3.01 eV and indirect band gap of 2.91 eV.

(Received October 8, 2013; Accepted January 10, 2014)

Keywords: Chalcogenides, Semiconductors, Composites Powders, Ionic Exchange.

1. Introduction

The chalcogenides exhibit various properties that are of considerable theoretical and practical importance. The tellurium and selenium are the most electronegative nonmetals of the chalcogenides group, with relatively high-ionization energies, and relatively strong elementelement bonds tending to form monoatomic and polyatomic anions[1]. The study of chalcogenides combined with IB group metals, has been of considerable interest [2]. The chemistry of Se and Te compounds has developed moderately; various factors have contributed to the increase interest in the chemistry of Se and Te, for example, the development of new suitable synthesis methodologies that avoid the use of noxious reagents. However, the most important is the great variety of technological applications that can be found for these compounds [1]. Copper chalcogenides presents numerous applications in devices such as solar cells, super ionic conductors, photo-detectors, photothermal conversion, electroconductive electrodes, microwave shielding coating, etc.[3]

^{*} Corresponding author: milka@cifus.uson.mx

In this work we focused in Copper selenide (CuSe) and copper telluride (CuTe) that are semiconductors I-VI. As examples of the wide variety of properties manifested by these materials are cuprous selenide (Cu_{2-x}Se) and cuprous telluride (Cu_{2-x}Te) as p-type extrinsic semiconductors in the solar cell production. Furthermore, both present direct and indirect band gaps, CuSe has been reported with a direct band gap in the range of 2 to 3 eV [4] and indirect band gap between 1.1 to 1.5 eV [5] Copper selenide has also been reported to possess a direct band gap of 4 eV [6]. Meanwhile CuTe has an indirect bandgap of 3.092 and 3.230 eV for nanowires [7] of 100 and 50 nm of length and a direct bandgap of 3 eV [8]. Moreover, the dichalcogenides CuSe₂ and CuTe₂ are superconductors at low temperatures [9]. We have described the procedure to obtain CuTe and CuSe by ionic exchange described by the following equations:

$$Cu(NO_3)_2 + Q[Te] ----> CuTe + 2OH^-$$
(1)

$$Cu(NO_3)_2 + Q'[Se] ----> CuSe + 2OH^-$$
(2)

Where Q[Te] and Q'[Se] are designed to describe the source of tellurium and sellenide, respectively, the chemical form of these complexes has been used by others researchers [10]. Next the formulations of Q and Q' are described.

2. Experimental details

Q: Te ions formulation.

The Q solution was prepared by mixing 2ml of rongalite 1M, 2ml of deionized water, 2 ml of sodium hydroxide 2M and 30 mg of tellurium. The mixed solution was heated until the solution turned purple.

Q': Se ions formulation.

The Q' solution was obtained with the same conditions of Q, but the difference is ammonium hydroxide was used instead of sodium hydroxide, and 30 mg selenide was used rather than tellurium. The mixture was heated until the solution was clear.

Powder Synthesis of CuSe and CuTe.

Copper selenide and copper telluride compounds were formed from 2 ml of copper nitrate aqueous solution 0.3 M and 2 ml of Q' or Q solution for selenide or telluride, respectively. The solutions were mixed and stirred vigorously at 25° C resulting in a dark precipitates. Those were collected and washed with pure water by centrifugation and dried in desiccator for 24 h.

The Raman spectroscopy was done using a system Horiba Jobin Yvon Spectrometer MicroRaman with source laser excitation and detector of 1024 pixels with a CCD High sensitivity, mounted in an Olympus microscope BX41TF with spatial resolution $<1 \mu$ m. The lasers used were three excitation ranges of 532, 638 and 785 nm, with spectral resolutions of 1.8 cm-1 / pixel (532nm) and 1.1 cm-1/pixel (785 nm). The Control laser power increments are 100%, 50%, 25%, 10%, 1% and 0.1%. The laser beam was focused with a 50X objective over a 2 micron spot on the sample, and Raman scattered beam was captured with the same objective. UV-vis spectra were performed with a UV-vis lambda 2 spectrophotometer; a XPS Perkin-Elmer, Phi-5000 model, was used to study the chemical composition of these samples. The morphology and EDS of the samples was investigated by high resolution transmission electron microscopy, HRTEM, using a JEOL 5400LV.

3. Results

In Fig. 1 the intense sharp Raman band at 258 cm⁻¹ has been generally attributed to binary copper selenides (CuSe, Cu_{2-x}Se) [11]. Moreover, one possible set of assignments is as follows: the band at 618 cm⁻¹ may be assigned to the $(SO_4)^{2-}$ bending mode and the band at 1067 cm⁻¹ is assigned to the $(SO_4)^{2-}$ antisymmetric stretching mode [12].



Fig. 1. Raman dispersion signal peaks obtained for the Cu-Se composite, where three frequencies have been identified by references.

In Fig. 2 the Raman spectrum the bands at 411, 438 and 471 cm⁻¹ for teineite (CuTeO₃·2H₂O) may be assigned to the E bending mode of $(TeO_3)^{2-}$, a possible assignment for the band at 775 cm⁻¹ would be antisymmetric stretching mode of TeO_4 . Typically the Raman band at 995 cm⁻¹ is associated to the symmetric stretching mode of $(SO_4)^{2-}$, also the sharp Raman band at 1062 cm⁻¹ is due to the antisymmetric stretching mode of $(SO_4)^{2-}$ [13]. Is important to remark that typically the lattice vibrations appear from 10 to 200cm⁻¹ region and the metallic with oxygen atom interaction are presented at the 200 to 450cm⁻¹ region [13].



Fig. 2. Raman dispertion signals peaks obtained for the Cu-Te composites, were indicated six frequencies values also by references.

The Fig. 3 presents the obtained information of the CuSe compound by X-ray photoelectron spectroscopy analysis, were the binding energies of Se 3d and Cu $2p^3$ of 53 eV and 953 eV, respectively. The peak value for Se 3d was attributed to an oxidation -2 for CuSe in

reference [14]. The kinetic energy of Cu L_3vv peak is 965.5 eV, therefore, the value of the modified Auger parameter is 995.5 eV, which can be used to differentiate it from CuSe and Cu₂Se, and the modified Auger parameter is close to that of Cu(I), this XPS feature should arise from main Cu(I) and diminish Cu(II) valence states. The chemical composition of this material can be deduced as CuSe with copper in the +2 oxidation state.



Fig. 3. XPS survey for cooper-selenium composite, while the inset depicts the selenium presence.

Also, in Fig. 4 the maxima for Te 3d5 corresponding to the binding energy value of 575.5 eV, which show the presence of telluride ion, while the peak in 587 eV corresponds to TeO₂ or Te (IV). In other words, the lower binding energy corresponds to the oxidation state Te^{2-} and the higher one to oxides, where the oxidation state is Te^{4+} . So the Te 3d region shows that the valence of Te is -2, while the Cu 3p region show valence for the copper of +1.



Fig. 4. XPS survey for the copper-tellurium composite, while the inset depicts two peaks of tellurium.

The morphology of copper selenide and copper telluride were investigated by TEM, the images are shown in Fig. 5 where it is depicted a 200 nm scale. For copper selenide it is observed that the particles are aggregated and indistinguishable from each other, while copper telluride presents a nanocaterpillar.

Beside each TEM contrast image is displayed the diffraction pattern corresponding, which indicates orthorhombic structures for both samples. Because the interplanar distances 3.208 A, 3.026 A, 2.029 A and 1.906 are characteristic of this type structure for the $Cu_{2-x}Se$ according to JCPDS card number 27-0184, and d = 3.514 A is characteristic for CuTe from JCPDS card number 22-0252.



Fig. 5. Micrographs of Cu-Se and Cu-Te composites, the up pair corresponds to the Cu-Se composite, where to the left it is shown a representative contrast image and to the right a higher magnification. The down pair corresponds to the similar for Cu-Te compound.

In order to examine the optical properties of the copper selenide and copper telluride compounds, a room temperature UV-Visible absorption measurement was made. The absorption spectra of copper selenide and copper telluride compounds are shown in Fig. 6 and Fig. 7, respectively. Those correspond to direct band gaps of 2.79 eV and 3.01 eV, and indirect band gaps of 1.36 and 2.91 eV for the CuSe and CuTe respectively. The direct band gap is determined using absorption spectrum through the Tauc-relation [14] as given by:

$$\alpha h v = A (h v - E_g)^n \tag{3}$$

where α is the absorption coefficient, *h* is the Planck constant, *v* is the frequency, A is a constant, E_g is the energy band gap and n = $\frac{1}{2}$ for direct band gap and n = 2 for indirect band gap. The value of direct band gap is obtained by extrapolating linear portion of the curve $(\alpha hv)^2 = 0$, by the other hand, the indirect band gap was obtained of $(\alpha hv)^{1/2} = 0$, and the determination for this gap is founded extrapolating linear too. The ultraviolet absorption spectrums were measured using double distilled water as reference media.



Fig. 6. Absorption response of the CuSe composite, left inset corresponds to the direct bandgap plot and right inset corresponds to indirect bandgap.



Fig. 7. Absorption response of the CuSe composite, left inset corresponds to the direct bandgap calculation and right inset corresponds to indirect bandgap.

4. Conclusions

This research provide a simple way to synthetize interesting binary semiconductors compounds such as copper selenide and copper telluride, which were identified by Raman spectroscopy. It is important to remark that the chemical reactions were achieved at room temperature. Another characterization studies could evidence traces of impurities, for instance we could not be to identify all the peaks or signals of Raman spectra. The contrast images TEM proof the crystalline nature with orthorhombic geometry.

Acknowledgments

We want to give thanks to Roberto Mora Monroy for the technical support in the XPS measurements.

References

- [1] F. A. Devillanova, Handbook of chalcogen Chemistry: New perspectives in sulfur, selenium and tellurium. (2007).
- [2] F. Moure-Flores, J.G. Quiñones-Galvan, A. Guillén-Cervantes, A. Hernández-Hernández, M.L.Olvera, J. Santoyo-Salazar, G. Contreras-Puente, M. Zapata-Torres, M. Meléndrez-Lira, Surface & Coatings Technology, 217, 181 (2013).
- [3] V. J. Fulari, V. P. Malekar, S.A. Gangawane, Progress In Electromagnetics Research C, 12, 53–64 (2010.
- [4] G. Statkut, I. Mikulskas, A. Jagminas, R. Tomas, I. Unas, Optical Materials 30, 743 (2008).
- [5] A. Zhang, Q. Ma, Z. Wang, M. Lu, P. Yang, G. Zhou, Materials Chemistry and Physics, 124, 916 (2010).
- [6] D. Patidar N. S. Saxena Journal of Crystal Growth 343, 68 (2012).
- [7] S. Kumar, V. Kundu, A. Vohra, S. K. Chakarvarti, J Mater Sci: Mater Electron 22, 995 (2011).
- [8] Y. Jiang, B. Xie, Wu, J., Yuan, S., Wu, Y., Huang, H., and Qian, Y., Journal of Solid State Chemistry 167, 28 (2002).
- [9] D. J. Chakrabarti, D. E. Laughlin, Bulletin of Allow Phase Diagram, Vol. 2, No. 3. (1981).
- [10] M., Sotelo-Lerma, R. A., Zingaro, S. J., Castillo, Journal of Organometallic Chemistry, 623, 81 (2001).
- [11] J.H. Shi, Z.Q. Li, D.W. Zhang, Liu Q.Q., Sun Z., Huang S.M. Progress in Photovoltaics: Research and Applications, 19, 160 (2011).
- [12] R.L. Frost, E.C. Keeffe, Journal of Raman Spectroscopy, 40, 42 (2009).
- [13] R.L. Frost, E.C. Keeffe, Journal of Raman Spectroscopy, 40, 128 (2009).
- [14] M. Lakshmi, K. Bindu, S. Bini, K.P. Vijayakumar, C. Sudha Kartha, T. Abe, Y. Kashiwaba, Thin Solid Films 386, 127 (2001)