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## Organic Functionalization Of Gallium Oxy-Hydroxide And Gallium Oxide And The Influence On The Band Gap Energy Measured By UV-Vis Spectroscopy.

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### ABSTRACT

Ga<sub>2</sub>O<sub>3</sub> is one semiconducting oxide with high chemical stability. A common precursor of this compound is a partial hydroxide form, GaOOH. The band gap energy of these both compounds was determined from UV-vis data and assessed after exposing the powders to solutions of organic compounds (urea, sodium dodecyl sulfate, phenylphosphonic acid and adipic acid). This solely exposition at room temperature favored the adsorption of the organic molecules onto the surface of both semiconducting materials, especially onto GaOOH, which enabled the adsorption through hydrogen bonds (as determined by infrared data) and consequently, this compound underwent a higher change in the band gap energy compared with Ga<sub>2</sub>O<sub>3</sub>.

**Keywords:** Gallium oxide, Functionalization, GAP, Tunability

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## INTRODUCTION

Among several semiconducting materials, binary compounds of gallium like nitrates and oxides have attracted the attention of scientists and developers of technology since they present a wide range of band gap values and high chemical and thermal stability (1). In the case of gallium oxides, they have been proposed to produce photocatalyst, photodetectors, solar-blind UV cameras, electrodes for sulphate quantification and barriers to avoid bacterial growth, among others (1–5).

On the other hand, functionalization of materials provides a way to modify or tune properties by either chemical physical or biological reactions (6). In gallium binary compounds, recent research has been conducted on GaN by functionalizing with amino groups and even with biomolecules like peptides (7,8). Regarding functionalization of gallium oxides, a couple of papers are reported: one is a theoretical study demonstrating that the functionalization of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> with carboxylic acids is possible and that alcohols and water are retained by H bonds (9); and the second describes an attempt to functionalize Ga<sub>2</sub>O<sub>3</sub> with dodecanoic acid and lysine. Even though such functionalization is not demonstrated, biocide assays indicated that the dodecanoic acid and lysine treatments improve the antibacterial activity (1). Both reports demonstrate, anyway, that functionalization of gallium occurs and the chemical properties are modified.

In this work, we functionalize gallium oxide and gallium oxyhydroxide particles with four organic molecules and explore the band gap energy determined by UV-vis spectroscopy with the aim to detect if functionalization is capable to affect such band gap energy. The organic compounds were selected considering the most common functional groups present in biological life and commercial compounds, such as –NH<sub>2</sub> in urea, –SO<sub>4</sub><sup>-</sup> in sodium dodecyl sulfate, –PO<sub>3</sub>H<sub>2</sub> in phenyl phosphonic acid and –COOH in adipic acid.

## METHODOLOGY

### *Gallium oxyhydroxide and gallium hydroxide synthesis*

A solution of Ga(III) was prepared by placing 1.5014 g of metal gallium (Sigma-Aldrich, 99.99%) in a round flask and mixed with 20 mL of 35% HNO<sub>3</sub> solution under an air extractor. The flask was immersed in a glycerin bath and heated at 60 °C under constant stirring to promote gallium oxidation. After three days a colorless solution was obtained and this was transferred to a volumetric flask and mixed with deionized water to complete a volume of 250 mL. Thereafter, 25 mL of Ga(III) were titrated with 14% ammonia solution and the pH. A white precipitate appeared at pH 3.5 and titration was stopped at pH 4.0 where the highest turbidity was observed. If pH is increased, the powder disappears due to hydrolysis. The powder was separated by decantation, washed with deionized water and dried at 80 °C. This powder was labeled as GaOOH once this is the compound commonly obtained from the reaction of Ga(III) solutions with a base (10,11).

Part of the GaOOH sample was calcined at 700 °C for 5 h in order to dehydrate the sample and produce the oxide (Ga<sub>2</sub>O<sub>3</sub>) (11). Both oxyhydroxide and oxide were prepared in duplicated experiments.

### *Functionalization*

The functionalization step was conducted by incubation (1,12). Firstly, 0.05 M solutions of urea (U), sodium dodecylsulfate (DDS), phenyl phosphonic acid (PP) and adipic acid (Adip) were prepared in deionized water (18 M-ohm). Then, 50 mL of these solutions were mixed with 0.500 g of GaOOH or (Ga<sub>2</sub>O<sub>3</sub>) and stirred at 27 °C for 24 h. Thereafter, the stirring was stopped and liquid phases were removed. The white powders were washed with deionized water and dried in an oven at 60 °C for 24 h. GaOOH and (Ga<sub>2</sub>O<sub>3</sub>) were labeled with Urea, SDS, PP or AA regarding the organic solutions where they were immersed. The effect of the concentration was studied with adipic acid in the functionalization of GaOOH once these two compounds produced the largest change in the band gap energy. The acid solutions were prepared at 5x10<sup>-2</sup>, 5x10<sup>-3</sup> and 5x10<sup>-4</sup> M.

### Characterization

The powder X-ray diffraction patterns were acquired with a Panalytical-Empyream diffractometer using  $\text{Cu}_{K\alpha}$  radiation (0.15418 nm) produced at 45 kV and 40 mA. Samples were scanned with steps of 0.02 degrees and exposition of 30 seconds per step. Infrared (IR) spectra were collected in the reflectance mode with a ThermoScientific spectrometer model NICOLET iS5 iD5 ATR using resolution of  $4\text{ cm}^{-1}$ . The UV-vis spectra were obtained with a ThermoSCIENTIFIC spectrometer model GENESYS 10S UV-Vis. The powder samples were weigh (20 mg) and mixed with 6mL of deionized water under sonication. This suspension was diluted 1:20 and sonicated for 20 minutes more and immediately read in the spectrometer at a resolution of 2 nm. The spectra were threated through the Tauc equation:  $\alpha hv = (hv - E_g)^m$ , where  $\alpha$  is the measured absorbance,  $h$  the Plank's constant,  $v$  the frequency,  $E_g$  the band gap energy and  $m$  assumes the value of  $\frac{1}{2}$  for direct band gap calculation (13,14). The linear component obtained after plotting  $(\alpha hv)^2$  versus  $hv$  (13,14).

## RESULTS AND DISCUSSION

### Solid state analysis

The powders obtained by precipitation with the alkaline solution presented a diffractogram (Figure 1) that matched with the profile recorded in the International Centre for Diffraction Data (ICDD) card number 06-0180. This corresponds to gallium oxyhydroxide with composition  $\text{GaOOH}$ . Regarding the XRD profiles of the powders obtained by calcination in duplicated experiments, they matched with the profile of the ICDD card number 43-1012 of an oxide with composition  $\text{Ga}_2\text{O}_3$ . The oxyhydroxide and the hydroxide were synthesized twice and the diffractograms of the replicates produced the same patterns, thus confirming reproducibility.

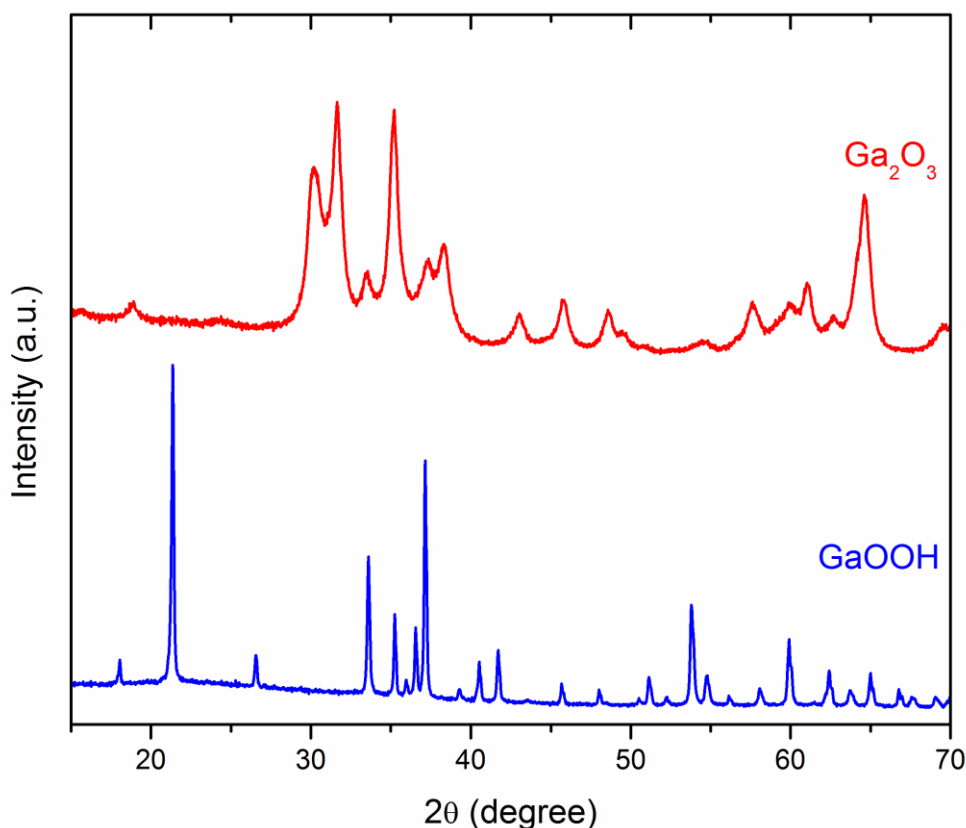
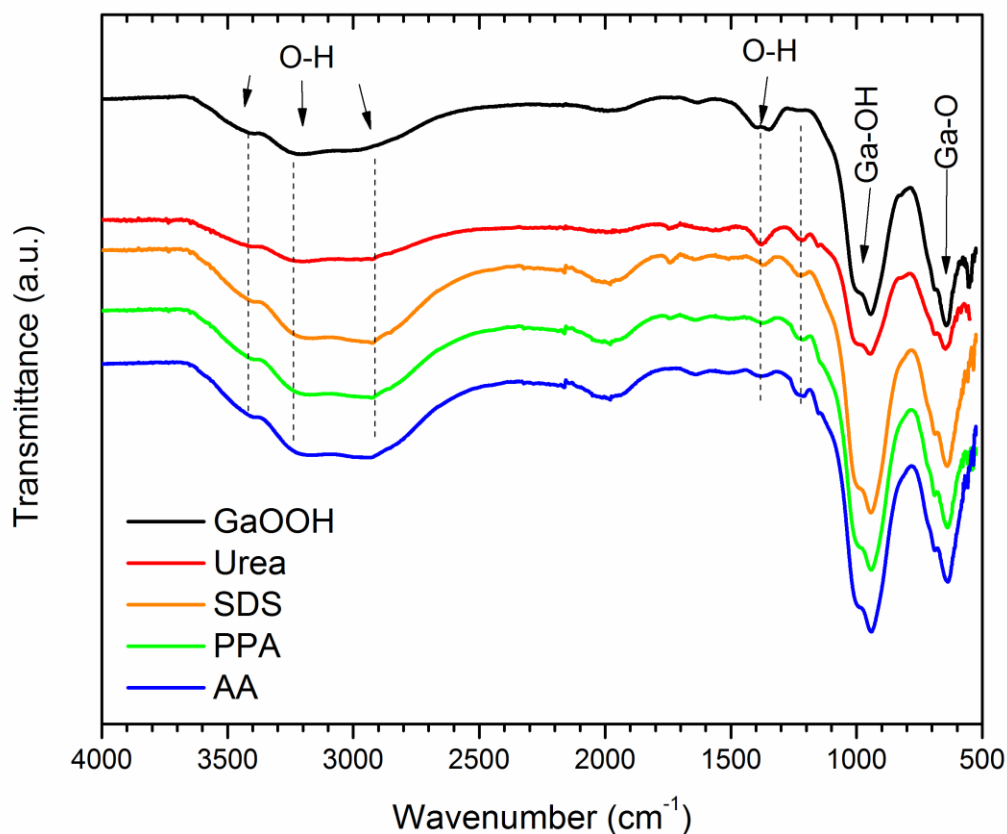


Figure 1: X-ray diffraction profiles of the  $\text{GaOOH}$  sample prepared by precipitation and the  $\text{Ga}_2\text{O}_3$  obtained by a subsequent calcination.

The infrared spectra in Figure 2 corresponds to samples of GaOOH treated in solutions with different organic molecules. The pristine GaOOH sample presented transmittance bands between 3500 and 2900  $\text{cm}^{-1}$  of O-H stretching modes (15), 1030 and 950  $\text{cm}^{-1}$  of the Ga-OH bending mode (15,16) ; a band of H-O stretching at 1315  $\text{cm}^{-1}$  (17) and an overtone signal around 2000  $\text{cm}^{-1}$  (18). The flexion of Ga-O-Ga bridges produces the band at 650  $\text{cm}^{-1}$  (15).

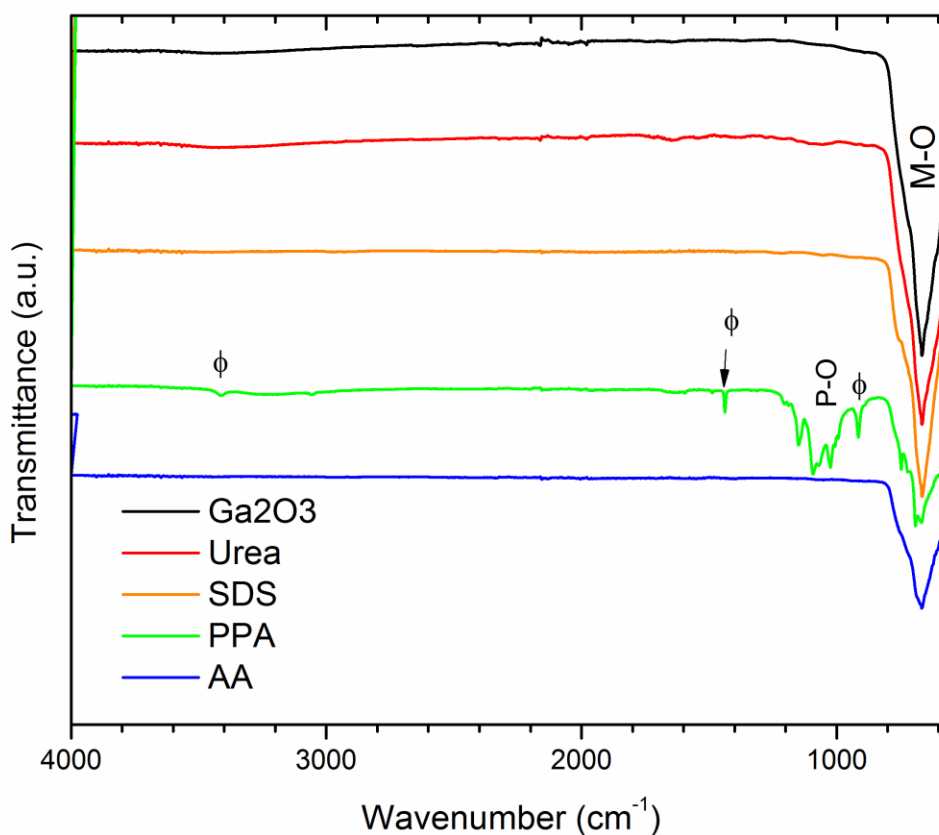


**Figure 2: Infrared spectra of GaOOH and the functionalization products.**

After the functionalization reactions there are not evident bands from the organic molecules. Although a set of bands are observed between 1800 and 1100  $\text{cm}^{-1}$ , these cannot be assigned to the organic fraction, as they appear at the same wavelength in all the samples regardless the functionalizing molecule. If the organic molecules are not evidenced by infrared spectroscopy, the concentration in this samples must be below 5% according to calibration curves conducted with our spectrometer.

The bands corresponding to Ga-OH, Ga-O-Ga and O-H are retained, indicating that the composition is maintained. However, the weak band assigned to the H-O stretching vibration at 1315  $\text{cm}^{-1}$  (17) becomes narrower, suggesting that a this groups is responsible for retaining the organic molecules as demonstrated in theoretical reports (9).

Regarding the infrared spectrum of the series prepared with  $\text{Ga}_2\text{O}_3$ , an intense signal is observed at 665  $\text{cm}^{-1}$  produced by the Ga-O-Ga stretching mode (15). Except in the PPA derivative, no other signals are observed indicating a very low content of the organic compounds. The PPA product contains intense bands related to the P=O and O-P-O stretching modes around 1087  $\text{cm}^{-1}$  (19) as well as bands from the aromatic ring identified with  $\phi$  within figure 3. The high intensity indicates that PPA is readily adsorbed by gallium oxide particles.



**Figure 3: Infrared spectra of Ga<sub>2</sub>O<sub>3</sub> and the functionalization products.**

UV vis spectra of all the samples were treated with the Tauc equation to obtain the  $E_g$  values and assess the effect of functionalization. The resulting plots are presented in figure 4. The duplicated experiments revealed that both GaOOH and Ga<sub>2</sub>O<sub>3</sub> presented  $E_g = 5.2$  eV (Table 1). Several semiconducting oxides have been proposed as sensors of gases and the resulting devices measure conductivity changes against exposition to gases like CO, CO<sub>2</sub> and propane (20,21). The current proposal is to determine if the band gap energy of GaOOH and Ga<sub>2</sub>O<sub>3</sub> is sensitive enough to detect, at least qualitatively, the presence of organic molecules. The estimated value for the band gap energy of GaOOH ( $E_g = 5.2$  eV) is in excellent agreement with reports in literature (22,23), on the other hand, the reported  $E_g$  values for Ga<sub>2</sub>O<sub>3</sub> oscillate between 4.8 and 5 eV (24–26), which differs with the value obtained in this work. The higher band gap value can be associated to quantum confinement due to the presence of small crystals. As it can be seen in figure 1, the XRD pattern for the Ga<sub>2</sub>O<sub>3</sub> sample shows broad peaks, the broadening of the peaks is an effect of crystal size reduction. In fact, the size of crystal determined through the Scherrer equation  $D = 0.9\lambda/\beta \cos\theta$  (where  $D$  is the average grain size,  $\theta$  and  $\beta$  are the diffraction angle and width of a reflection peak (27)) indicate that the crystallite size of GaOOH ranged from 41 to 57 nm and decreased to 9 to 28 nm in Ga<sub>2</sub>O<sub>3</sub>.

This  $E_g$  value of GaOOH was reduced from 5.2 to 4.3, 4.6, 3.7 and 4.4 eV after exposition to Urea, SDS, PPA and AA, respectively, whereas the  $E_g$  of Ga<sub>2</sub>O<sub>3</sub> (5.2 eV) was also decreased to 5.1, 4.9, 4.9 and 4.8 eV in the same sequence of organic compounds. More pronounced changes were induced in the GaOOH powder where  $\Delta E_g$  values ranged from 0.7 eV (with DSD) to 1.6 eV (with AA), whilst  $\Delta E_g$  in Ga<sub>2</sub>O<sub>3</sub> presented lower differences from 0.1 eV (with Urea) to 0.4 (with PPA).

A possible reason for the stronger change in the GaOOH sample is the higher ability to form H bonds (9), and thus stronger attraction results between the organic molecules and the GaOOH surface which may introduce deep energy levels within the band gap generating allowed transitions at lower energies. Detection

of organic molecules based on band gap changes provide an alternative method to design detectors to those systems based on resistivity (20,21).

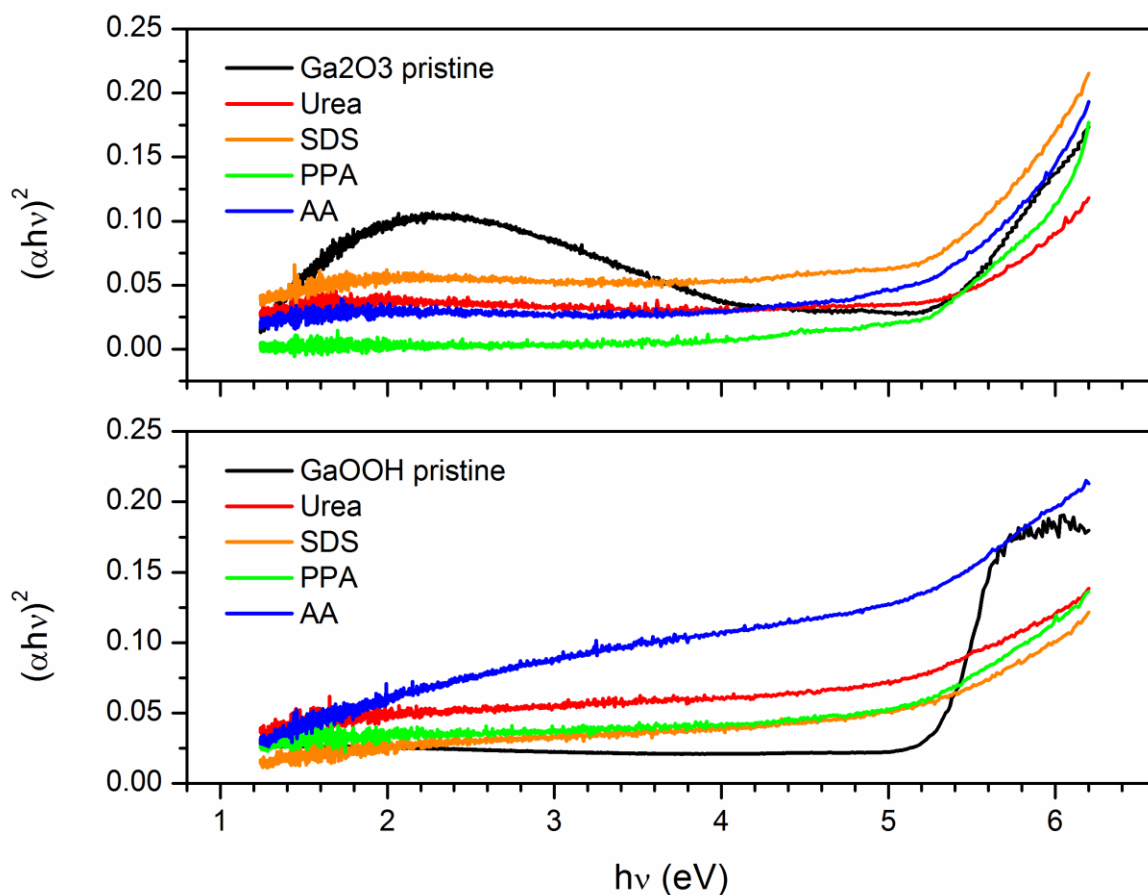


Figure 4: Tauc plots from the UV-vis spectra of GaOOH, Ga<sub>2</sub>O<sub>3</sub> and their respective functionalization products with organic molecules.

Table 1: Band gap energy ( $E_g$ ) values obtained after functionalization of GaOOH ( $E_g = 5.2$  eV) and Ga<sub>2</sub>O<sub>3</sub> ( $E_g = 5.2$  eV).

Functionalizing agent	GaOOH $E_g$ (eV)	GaOOH $\Delta E_g$ (eV)	Ga <sub>2</sub> O <sub>3</sub> $E_g$ (eV)	Ga <sub>2</sub> O <sub>3</sub> $\Delta E_g$ (eV)
Urea	4.3	1.0	5.1	0.1
SDS	4.6	0.7	4.9	0.3
AA	3.7	1.6	4.9	0.3
PPA	4.4	0.9	4.8	0.4

However, consideration on concentration must be taken into account. The data in Table 2 correspond to the band gap energy changes detected after exposition in different logarithmic concentrations of AA. Fluctuations are observed from  $5 \times 10^{-4}$  to  $5 \times 10^{-2}$  M since there change in the  $E_g$  is not proportional to the AA concentration, in fact, the medium concentration presented the highest  $E_g$  value. Due to this irregular result, the powders were analyzed in a different spectrometer, instead of the Genesys 10S model from Thermo Scientific, an older Genesys 10 model from Thermo Spectronic was used, and in this case, the increase in concentration produced a larger  $E_g$  value. The interesting results here is that the lower concentrations,  $5 \times 10^{-4}$  and  $5 \times 10^{-3}$  M, produce mean  $E_g$  values with the largest standard deviation (0.49 and 0.64), while the standard deviation in the mean value with the most concentrated solution was only 0.01. Therefore, the use of these powders are reliable at concentrations above  $10^{-3}$  M, where likely the population of functionalizing molecules is large enough to uniformly cover all the particles.

**Table 2: Band gap energy ( $E_g$ ) after functionalization of GaOOH ( $E_g = 5.2$  eV) with adipic acid at different concentrations**

	$E_g$ (eV) after immersion in AA		
	$5 \times 10^{-4}$ M	$5 \times 10^{-3}$ M	$5 \times 10^{-2}$ M
Genesys 10S, Thermo Scientific spectrometer	5.43	5.48	5.40
Genesys 10, Thermo Spectronic spectrometer	5.36	5.39	5.41
Mean value	5.39	5.43	5.40
Standard deviation	0.049	0.064	0.01

### CONCLUSIONS

The band gap energy of GaOOH and Ga<sub>2</sub>O<sub>3</sub> were 5.2 eV for both compounds. The exposition of these powder compounds to solutions of organic molecules reduced such energy. More marked differences, from 0.7 to 1.6 eV, were detected in GaOOH where the attaching of organic molecules is more favorable through hydrogen bonds. Although differences in Ga<sub>2</sub>O<sub>3</sub> ranged from 0.1 to 0.4 eV, the values are detectable, thus evidencing that detection of organic molecules is possible if enough concentration is present to uniformly functionalize all the particles.

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### REFERENCES

- [1] Murthy PS, Venugopalan VP, Sahoo P, Dhara S, Das A, Tyagi AK, et al. IEEE; 2011: 490–493.
- [2] Girija K, Thirumalairajan S, Patra AK, Mangalaraj D, Ponpandian N, Viswanathan C. *Curr Appl Phys* 2013; 13(4): 652–658.
- [3] Kumar S, Dhara S, Agarwal R, Singh R. *J Alloys Compd* 2016; 683: 143–148.
- [4] Liu XZ, Guo P, Sheng T, Qian LX, Zhang WL, Li YR. *Opt Mater* 2016; 51: 203–207.
- [5] Pandey B, Cox CB, Thapa PS, Ito T. *Electrochim Acta* 2014; 142: 378–385.
- [6] Treccani L, Yvonne Klein T, Meder F, Pardun K, Rezwani K. *Acta Biomater* 2013; 9(7): 7115–7150.
- [7] Stine R, Simpkins BS, Mulvaney SP, Whitman LJ, Tamana CR. *Appl Surf Sci* 2010; 256(13): 4171–4175.
- [8] Estephan E, Larroque C, Cuisinier FJG, Bálint Z, Gergely C. *J Phys Chem B* 2008; 112(29): 8799–8805.
- [9] Bermudez VM. *Langmuir*. 2008; 24(18): 12943–12952.
- [10] Li D, Wang F, Zhu JF, Liu DW, Wang XF, Xiang LY. *Mater Sci Forum* 2011 ; 675–677: 251–254.
- [11] Zhao Y, Yang J, Frost RL. *J Raman Spectrosc* 2008; 39: 1327–1331.
- [12] Arízaga GGC, Oviedo MJ, López OEC. *Colloids Surfaces B Biointerfaces* 2012; 98C: 63–71.
- [13] Li X, Zhu H, Wei J, Wang K, Xu E, Li Z, et al. *Appl Phys A Mater Sci Process* 2009; 97: 341–344.
- [14] Srivastava A, Misra KP. *Appl Phys A*. 2014; 117: 917–926.
- [15] Liu X, Qiu G, Zhao Y, Zhang N, Yi R. *J Alloys Compd* 2007; 439(1–2): 275–278.
- [16] Lee I, Kwak J, Haam S, Lee SY. *J Cryst Growth* 2010; 312(14): 2107–2112.
- [17] Reddy LS, Ko YH, Yu JS. *Nanoscale Res Lett* 2015; 10(1): 364.
- [18] Quan Y, Fang D, Zhang X, Liu S, Huang K. *Mater Chem Phys* 2010; 121(1–2): 142–146.
- [19] Xie J, Zhang K, Zhao Q, Wang Q, Xu J. *J Solid State Chem* 2016; 243: 62–69.
- [20] Guillén-Bonilla H, Flores-Martínez M, Rodríguez-Betancourt V-M, Guillén-Bonilla A, Reyes-Gómez J, Gildo-Ortiz L, et al. *Sensors* 2016; 16(2): 177.
- [21] Guillén-Bonilla A, Rodríguez-Betancourt V-M, Flores-Martínez M, Blanco-Alonso O, Reyes-Gómez J, Gildo-Ortiz L, et al. *Sensors* 2014; 14(9): 15802–15814.
- [22] Sinha G, Adhikary K, Chaudhuri S. *J Phys Condens Matter* 2006; 18(8): 2409–2415.
- [23] Wu S, Zhang J, Shi L, Tang S, Li Y, Jiang L, et al. *RSC Adv* 2014; 4(16): 8209.



- [24] Zhang J, Li B, Xia C, Pei G, Deng Q, Yang Z, et al. *J Phys Chem Solids* 2006; 67(12): 2448–2451.
- [25] Ju M-G, Wang X, Liang W, Zhao Y, Li C. *J Mater Chem A* 2014; 2(40): 17005–17014.
- [26] Mohamed M, Unger I, Janowitz C, Manzke R, Galazka Z, Uecker R, et al. *J Phys Conf Ser* 2011; 286(1): 012027.
- [27] Liu X, Pang R, Li Q, Lin J. *J Solid State Chem* 2007; 180: 1421–1430.