Dynamic Response of CoSb$_2$O$_6$ Trirutile-Type Oxides in a CO$_2$ Atmosphere at Low-Temperatures

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Abstract: Experimental work on the synthesis of the CoSb$_2$O$_6$ oxide and its CO$_2$ sensing properties is presented here. The oxide was synthesized by a microwave-assisted colloidal method in presence of ethylenediamine after calcination at 600 °C. This CoSb$_2$O$_6$ oxide crystallized in a tetragonal structure with cell parameters $a = 4.6495$ and $c = 9.2763$ Å, and space group $P4_2/mnm$. To prove its physical, chemical and sensing properties, the oxide was subjected to a series of tests: Raman spectroscopy, Scanning Electron Microscopy (SEM) and impedance (Z) measurements. Microstructures, like columns, bars and hollow hemispheres, were observed. For the CO$_2$ sensing test, a thick film of CoSb$_2$O$_6$ was used, measuring the impedance variations on the presence of air/CO$_2$ flows (0.100 sccm/0.100 sccm) using AC (alternating current) signals in the frequency-range.
0.1–100 kHz and low relative temperatures (250 and 300 °C). The CO2 sensing results were quite good.

**Keywords:** sensing properties; CoSb2O6; trirutile; chemical synthesis

1. Introduction

Due to environmental concerns, the constant monitoring of the gases emitted to the atmosphere is highly important. Therefore, intense research on the gas-sensors area is carried out nowadays, especially regarding sensors based on semiconductor materials, like the oxides SnO2, ZnO, TiO2, WO3, LaFeO3 and CoAl2O4 [1–7]. Such materials show interesting sensing properties, remaining at the same time chemically stable in the presence of polluting gases. In recent years, oxides with a trirutile-type structure, like CoSb2O6 [8,9] and ZnSb2O6 [10,11], are being studied for gas-sensing applications with very good results. These results are mainly attributed to the nano-sized structure of the trirutile oxides, which therefore determines the best synthesis process (route) to produce them [9]. The ceramic method for the synthesis of oxides has been extensively used; however, this conventional process involves some disadvantages, for instance, it is necessary to heat the sample at elevated temperatures for a long time. Such treatment results in inhomogeneous materials, no control of the particle size and a decrease of the surface area. In order to overcome these problems, wet chemical routes can also be successfully employed, at relative low temperatures, yielding nanoparticles with unique microstructural features [12–14].

In addition, the response of a sensor in polluting gases atmospheres is strongly related to the chemical reactions occurring on the oxide surface; therefore, the microstructure determines the conversion efficiency of chemical interactions into electrical signals. So, it is very important to synthesize materials with optimal morphologies [1,15]. In this work we implemented a chemical synthesis route (the microwave-assisted colloidal method) to produce the CoSb2O6 oxide for gas sensing purposes. The employed synthesis route was found very convenient because a good stoichiometry control was possible, influencing positively on the microstructural characteristics of the oxide.

2. Experimental Section

2.1. Synthesis of Trirutile-Type CoSb2O6 Oxide

The trirutile-type structure CoSb2O6 oxide was synthesized based on the procedure described in [8,9]. However, in this work, these reagents were used: SbCl3 (Sigma-Aldrich), Co(NO3)2·6H2O (Mallinkrodt), 1 mL of ethylenediamine, and 5 mL of ethanol (Golden Bell). The resulting solution was evaporated by means of a microwave oven (JES769WK General Electric) at low power (180 W at 10–20 s intervals; the absorbed energy was calculated to be close to 85 kJ). The obtained precursor material was dried at 200 °C in static air for 8 h, then calcined in a muffle (Novatech) at 600 °C in static air for 6 h. In this process, a heating rate of 100 °C/h was employed.
2.2. Characterization of CoSb_2O_6 Powders

The calcined powders were analyzed by X-ray diffraction (XRD) at room temperature, using a D500 Siemens diffractometer (Siemens, Munich, Germany) with a Cu-Kα radiation (λ = 0.1518 nm). The 2θ scanning range was from 10° to 70° with a velocity of 1° min^{-1}. The powders were also analyzed by Raman spectroscopy (Renishaw, Inc, Schaumburg, IL, USA) using a 1000B microRaman Renishaw system, calibrated with a silicon semiconductor with its characteristic Raman peak at 520 cm^{-1}. The laser (excitation wavelength of 830 nm) was focused on the surface of the powders (spot size of approximately 20 μm) by means of a Leica optical microscope (DMLM; Leica microsystems, Deerfield, IL, USA) integrated to the microRaman system. The radiation energy on the sample was 4.5 mW 60 s. The morphology of the CoSb_2O_6 powders was analyzed by scanning electron microscopy (JEOL JSM-6390LV; Jeol, Inc., Dearborn, MI, USA).

The electrical characterization was made through dynamic tests of the impedance variation using a thick film made of oxide powders, which were set inside of a controlled tube-type furnace at temperatures of 250 and 300 °C. The impedance measurements were made by the two-tips technique using a computer controlled (with LabView 8.6, National Instruments) (Agilent 4263B device; Agilent Technologies, Inc, Santa Clara, CA, USA). The flow of the synthetic air/CO_2 gases was controlled by a MKS 647C controller (MKS Instruments, Inc, Andover, MA, USA).

3. Results and Discussion

3.1. X-Ray Diffraction Analysis

Figure 1 shows an X-ray diffraction pattern of the powders prepared by the above described method.

Figure 1. X-ray diffraction pattern of CoSb_2O_6 powders calcined at 600 °C in air.
The diffractogram shows the presence of the main phase corresponding to CoSb$_2$O$_6$, which was identified using the file ICDD 203094. According to this card, the CoSb$_2$O$_6$ oxide crystallized in a tetragonal structure with cell parameters $a = 4.6495$ and $c = 9.2763$ Å, and space group $P4_2/mnm$ (136) [16], which indicates that the oxide belongs to the family of trirutile-type structures [17]. In addition, the width of the peaks in the diffraction spectra is an indication of crystals of nanometric size; the low noise level indicates that the sample possesses a high crystallinity [18]. The estimated crystal size according to the Scherrer equation [19] for the CoSb$_2$O$_6$ powders was around 41 nm. Furthermore, low intensity peaks identified through the ICDD 87234 file, reveal a secondary phase:

Co$_{2.33}$Sb$_{0.67}$O$_4$ [9], localized on the angular positions $2\theta = 17.8^\circ$, $2\theta = 29.5^\circ$, $2\theta = 36.2^\circ$, and $2\theta = 42^\circ$.

Several other synthesis methods have been used for the preparation of oxides with trirutile-type structure. Larcher et al. [20] synthesized trirutile-type ASb$_2$O$_6$ materials (A = Ni, Cu, Co), following the solid-state reaction method, obtaining the structures at 800 °C. Michel et al. [21] obtained the CoSb$_2$O$_6$ oxide employing the solution-polymerization method at 700 °C. From the present work, and comparing with other studies, it can be stated that the obtention of the CoSb$_2$O$_6$ oxide is very feasible at temperatures significantly lower than those used by the authors above mentioned, by means of the synthesis route proposed here (the microwave-assisted colloidal method).

### 3.2. Raman Spectroscopy Analysis

The Raman analysis (Figure 2 and Table 1) shows the vibrations modes $A_{1g}$, $B_{1g}$, $B_{2g}$ and $E_g$ at the range 190–800 cm$^{-1}$. Band $v_1$ has a mean intensity $\sim 194 \pm 3$ cm$^{-1}$ and is due to the vibrations of the crystalline network with $A_{1g}$ symmetry. Band $v_2$, at $\sim 478 \pm 3$ cm$^{-1}$, is due to the deformation vibration of the Co-O bond, also with $A_{1g}$ symmetry. Band $v_3$, at $\sim 518 \pm 3$ cm$^{-1}$, can be attributed to the combination of the stretching and coupling vibrations of the Sb-O bonds, with symmetry $E_g$. Band $v_4$, at $\sim 617 \pm 3$ cm$^{-1}$, is due to the asymmetric stretching vibration of the Sb-O bond, with symmetry $E_g$. Band $v_5$, at $\sim 641 \pm 3$ cm$^{-1}$, showing a high intensity, is due to the symmetric stretching vibration of the Sb-O bond, with $E_g$ symmetry. These results are in agreement with [22] and [23], and support the correct characterization of the oxide.

**Figure 2.** Raman spectrum of CoSb$_2$O$_6$ powders calcined at 600 °C in air.
Table 1. Vibration modes of the CoSb₂O₆ oxide.

| Mode | Raman Displacement (cm⁻¹) | Symmetry | Vibration Type                  | Molecular Bond |
|------|---------------------------|----------|---------------------------------|----------------|
| ν₁   | ~194 ± 3                  | A₁g      | Crystalline network             | Co-O           |
| ν₂   | ~478 ± 3                  | A₁g      | Deformation                     |                |
| ν₃   | ~518 ± 3                  | E₈g      | Stretching and Coupling         |                |
| ν₄   | ~617 ± 3                  | E₈g      | Stretching (asymmetric)         | Sb-O           |
| ν₅   | ~641 ± 3                  | E₈g      | Stretching (symmetric)          | Sb-O           |

3.3. Scanning Electron Microscopy Analysis

Figure 3 shows photomicrographs of the CoSb₂O₆ oxide at several magnifications: (a) 350X, (b) 370X, and (c) 700X. The discerned particle shapes are rectangular micro-bars with sizes: base ~28.5 µm, length ~42 µm and height ~13 µm. Around these bars, some smaller structures in form of micro-rods, growing in different directions, are also discernible. The micro-rods growth, with an estimated diameter of ~2.7 µm, is attributed to the increasing of the temperature and the effects caused by the ethylenediamine. These micro-rods tend to aggregate to form a hollow hemisphere (see image b). The granulate surface of the micro-rods is probably due to the released gases from organic material during the thermal decomposition in the oxide’s synthesis [24]. The size distribution of the micro-rods (also shown in Figure 3d) depicts a length range of 6–24 µm with a standard deviation of 3.4 µm and an average length of ~12.7 µm. The role of ethylenediamine in the formation of 1D structures of II–VI semiconductors, like nanorods and nanowires, has been discussed in previous works [25,26]. The ethylenediamine is incorporated first into the inorganic framework and then escapes from it to form particles of desired morphologies [26]. In this work, we found that the presence of ethylenediamine in the CoSb₂O₆ synthesis leads to the growth of micro-rods. In fact, we reported in a previous work [27] the obtention of trirutile-type MgSb₂O₆ with different morphologies, micro-rods and micro-plates among them, by the use of ethylenediamine.

Figure 3. SEM (scanning electron microscopy) images of CoSb₂O₆ powders at different magnifications: (a) 350X; (b) 370X; and (c) 700X; (d) length distribution of the micro-rods.
On the other hand, the preparation of different inorganic compounds by means of colloidal routes has been widely studied by Matijevic [28]. Some authors report the obtention of morphologies similar to those here reported, which originate from the growth process of stable nuclei of the colloidal systems [28,29]. These morphologies are in agreement with the crystallization principles proposed by LaMer and Dinegar [9,24,27,30].

3.4. Impedance Measurements and Gas Sensing Properties

To test the gas sensing properties of the CoSb$_2$O$_6$ oxide, a thick film (thickness ~500 μm) was employed for measuring its impedance variation in presence of air/CO$_2$ flows (0.100 sccm/0.100 sccm). Experiments at four frequencies (AC (alternating current) signals) were conducted in this study: 0.1, 1, 10 and 100 kHz, and at two different temperatures, namely, 250 and 300 °C. The process to perform the dynamic response experiments consisted of three stages: (1) for each frequency and temperature, synthetic air was flowed over the film’s surface during approximately 5 min in order to stabilize it; (2) a CO$_2$ flow was applied on the material, recording the impedance (|Z|) variations; (3) after one minute, synthetic air was flowed again over the thick film, returning the impedance |Z| to the initial state. Figure 4 shows the dynamic tests results of the CoSb$_2$O$_6$ oxide at 250 °C, and Table 2 shows the calculated variations. In all four tests (0.1, 1, 10 and 100 kHz), the magnitude of the impedance (|Z|) changes in an alternating manner when the gas flow changes from air to CO$_2$. These results reveal that the material exhibits sensitivity and repeatability in CO$_2$ detection. In particular, at the 0.1 kHz frequency, the change of the magnitude |Z| was ~3.23 kΩ on average (Figure 4a); while at the 1 kHz frequency, the recorded change was ~2.91 kΩ on average (Figure 4b). On the other hand, at the 10 kHz frequency, the magnitude of the impedance changes ~2.43 kΩ on average (Figure 4c); however, using a high frequency of 100 kHz, the magnitude of the impedance is reduced to an average value of ~1.71 kΩ (Figure 4d).

In addition, Figure 4 shows the fast response and recovery times recorded during the exposure to the CO$_2$ gas at 250 °C. The response times, measured at 90% of the full response, were 22.38, 21.56, 20.32 and 18.19 s at the frequencies 0.1, 1, 10 and 100 kHz, respectively, while the recorded recovery times were 21.36, 20.06, 19.06 and 17.95 s at the same frequencies, respectively (See Table 2).
these results, CoSb$_2$O$_6$ thick films respond faster and with a shorter recovery time at the higher frequency (100 kHz); however, upon increasing the frequency, smaller $|Z|$ values were registered.

Figure 4. Dynamic response of the CoSb$_2$O$_6$ oxide subjected to CO$_2$ flows at 250 °C and different frequencies: (a) 0.1 kHz; (b) 1 kHz; (c) 10 kHz; and (d) 100 kHz.

Table 2. Variations of the impedance measurement at 250 °C.

| Frequency (kHz) | Mean Impedance (kΩ) | Response Time (s) | Recovering Time (s) |
|----------------|----------------------|-------------------|---------------------|
| 0.1            | 3.23                 | 22.38             | 21.36               |
| 1              | 2.91                 | 21.56             | 20.06               |
| 10             | 2.43                 | 20.32             | 19.06               |
| 100            | 1.71                 | 18.19             | 17.95               |

Figure 5 shows the results of the dynamic tests on the CoSb$_2$O$_6$ oxide at 300 °C with the same frequencies and gases flows, and the calculated variations are shown in Table 3. Similar tendencies to those shown in Figure 4 were recorded. However, at 300 °C, the changes of the magnitude $|Z|$ were ~1.29, ~1.18, ~1.09 and ~0.921 kΩ, at the frequencies 0.1, 1, 10 and 100 kHz, respectively. In addition, the response and recovery times were reduced to values less than 20 s due to the effect of the temperature. In this case, the response times were 17.32, 16.30, 15.00 and 14.18 s, while the recovery times were 16.18, 15.00, 13.93 and 13.00 s at the same frequencies, respectively (see Table 3). Clearly, at higher temperatures and frequencies applied, the CoSb$_2$O$_6$ sensor exhibits faster response and shorter recovery times.
Figure 5. Dynamic response of the CoSb₂O₆ oxide subjected to CO₂ flows at 300 °C and different frequencies: (a) 0.1 kHz; (b) 1 kHz; (c) 10 kHz; and (d) 100 kHz.

Table 3. Variations of the impedance measurement at 300 °C.

| Frequency (kHz) | Mean Impedance (kΩ) | Response Time (s) | Recovering Time (s) |
|----------------|----------------------|-------------------|---------------------|
| 0.1            | 1.29                 | 17.32             | 16.18               |
| 1              | 1.18                 | 16.30             | 15.00               |
| 10             | 1.09                 | 15.00             | 13.93               |
| 100            | 0.921                | 14.18             | 13.00               |

To discern the effects of frequency and temperature on the CoSb₂O₆ ability to detect air/CO₂, Figure 6 shows graphically the above mentioned variations. Clearly, increasing the frequency and the temperature, the impedance drops considerably, which is a characteristic of semiconductor materials. At 250 °C, the average |Z| is 2.52 kΩ and at 300 °C, it is 1.12 kΩ. The oxide therefore behaves like a low-pass filter and can be modeled as a parallel RC circuit (see Figure 7). This circuit is made up of the alternating current (AC) source, a resistance (R) and a capacitor (C) [8]. In addition, the behavior of the dynamic response obtained at 250 and 300 °C can be reproducible. This suggests that this material can reliably be applied as a gas sensor under air/CO₂ flows [31].
Figure 6. Impedance $|Z|$ vs. frequency tests of the CoSb$_2$O$_6$ oxide at (a) 250 °C and (b) 300 °C with air/CO$_2$ flows.

Figure 7. Equivalent RC parallel circuit for the CoSb$_2$O$_6$ sensor.

Comparing the results of Figures 4 and 5 with those reported in previous works corresponding to the CoSb$_2$O$_6$ oxide, a better performance as gas sensor was obtained in the present work. For example, nanostructured CoSb$_2$O$_6$ microspheres have been synthesized employing a non-aqueous method in presence of n-dodecylamine [9]. These CoSb$_2$O$_6$ microspheres were sensitive to detect 400 ppm of CO$_2$ at 400 °C with a response time of 130 s and a recovery time of 22 s. Also, the variation in electrical resistance recorded was 130 $\Omega$. In addition, the dynamic response of CoSb$_2$O$_6$ prepared by solution-polymerization method has been reported [21]. In this paper, a CO$_2$ flow (100 cm$^3$/min) produces an increase in electrical resistance of 900 $\Omega$ in 3 min (410 °C). However, the CoSb$_2$O$_6$ oxide synthesized in this work exhibits good sensing properties at lower temperatures (250 and 300 °C) to those reported in the previous works. Additionally, a faster response, shorter recovery times, better repeatability and larger impedance changes were obtained. This gas response can be attributed to the microstructure found in this work, and its nanocrystalline nature.

Moreover, from Figures 4 and 5 the rise of $|Z|$ during the flow of CO$_2$ indicates a p-type semiconductor [31,32]. In general, the gas-sensing mechanism in semiconductor materials is based on the electric resistance change (conductance) produced by the electron transfer occurring during the chemical adsorption [32]. In the presence of a gas, such as the one used in this study (CO$_2$), electrons are provided to the oxide surface and they combine with holes. Therefore, the concentration of electrical charge carriers (holes) is reduced and the magnitude $|Z|$ increases. The process of CO$_2$ adsorption on metal oxide surfaces can involve the formation of several carbon species, such as
bicarbonate and carbonates [33]. These carbon species are removed when air is injected. Then, the magnitude $|Z|$ reached its original value.

Depending on the type of the semiconductor, the concentration of the charge carriers on the surface can be increased or decreased [34]. The thickness of the charged $L_S$ outer layer can be defined as [34]:

$$L_S = L_D \sqrt{\frac{eV_S^2}{kT}}$$  \hspace{1cm} (1)

where $L_D$ is the Debye length, $e$ is the charge of the electron, $V_S$ is the potential of the surface, $k$ is the Boltzmann constant, and $T$ is the temperature. Usually, the $L_S$ values are between 1 and 100 nm [34].

According to some authors, the charged outer layer mainly depends on the gas pressure and the gas concentrations. These results of the changing resistance value and the conductivity variation of the semiconductor can be consulted in [35]. Due to this, the conductivity strongly depends on the size of the crystal ($D$), thus giving rise to three possible scenarios [36]:

1. If $D \gg 2L_S$, the conductivity is limited by the Schottky barrier at the particle border; thus, the gas detection does not depend on the crystal size ($D$),
2. If $D = 2L_S$, the conductivity and the gas sensing depend on necks formed by the crystals, and
3. If $D < 2L_S$, the conductivity depends on the crystal size [36,37]. Based on these three scenarios, it can be said that the smaller the size of the particle during its synthesis, the greater the surface area obtained and, therefore, a better gas adsorption [34].

In addition, the good electric response of the CoSb$_2$O$_6$ under a controlled air/CO$_2$ flow can be to a great extent explained by the presence of microstructures obtained during the process of synthesis.

4. Conclusions

Desirable trirutile-type CoSb$_2$O$_6$ structures for gas-sensing applications, like micro-rods and micro-bars, were successfully prepared by a wet-chemical synthesis route at relatively low temperatures. The results of this work, regarding the sensing properties of the synthesized material, show that at different frequencies, the dynamic response improves under air/CO$_2$ flows. The CoSb$_2$O$_6$ thick films respond faster and with a shorter recovery time at higher temperatures and frequencies (100 kHz and 300 °C). Also, the results indicated that increasing the frequency, smaller $|Z|$ values were obtained. The uniformity of the dynamic tests reflects the good impedance response during the adsorption of the CO$_2$. According to this, the CoSb$_2$O$_6$ oxide is a strong candidate to be applied as an environmental gas sensor, especially when synthesized by our proposed method.

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Author Contributions

Verónica-María Rodríguez-Betancourt was the supervisor of the PhD work of the author (Alex Guillén-Bonilla), from which this study results and contributed with work on the Raman spectroscopy analysis and the writing of this article; Martín Flores-Martínez contributed with work on the XRD analysis; Oscar Blanco-Alonso contributed with work on the gas-sensing tests; Juan Reyes-Gómez contributed with work on the SEM; Lorenzo Gildo-Ortiz contributed on observations, recommendations, discussion and a critical review of the manuscript; Héctor Guillén-Bonilla contributed with work on the synthesis method and the writing of this article. All authors Guillén-Bonilla read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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