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# Prototyping a Gas Sensors Using $\text{CeO}_2$ as a Matrix or Dopant in Oxide Semiconductor Systems

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Additional information is available at the end of the chapter

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## Abstract

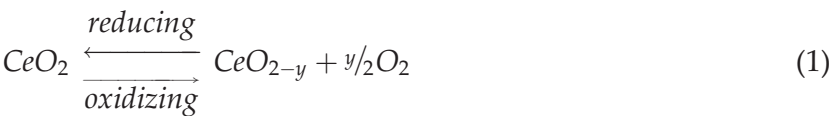
In this chapter, two important aspects of using  $\text{CeO}_2$  in the field of gas sensors are presented. Firstly, for  $\text{CO}_2$  detection in the range of 0–5000 ppm, a binary semiconductor oxides  $\text{CeO}_2\text{-Y}_2\text{O}_3$  was used. Secondly, as a dopants, in oxide semiconductor systems, used to detect the  $\text{NO}_2$ . In this case,  $\text{CeO}_2$  is used as a dopant in hybride composite, consisting of reduced graphene oxide/ $\text{ZnO}$ , in order to increase the sensibility in  $\text{NO}_2$  detection at low concentration in the range of 0–10 ppm. The structural and morphological characterization of sensitive materials by X-ray diffraction, SEM, adsorption desorption isotherms, thermal analysis and RAMAN spectroscopy are presented. Also, the sensing element of the sensor that detects the  $\text{NO}_2$  is achieved by depositing the nanocomposite material on the interdigital grid. The electronic conditioning signal from the sensing element is achieved by using a Wheatstone bridge together with an instrumentation operational amplifier.

**Keywords:** ceria oxide, yttrium oxide, zinc oxide, reduced graphene oxide, sensing element, electronic conditioning, X-ray diffraction, scanning electron microscopy

## 1. Introduction

Cerium represents one of the most abundant elements in the Earth's crust (66.5 ppm) than copper (60 ppm) or tin (2.3 ppm). Ce possesses an unique electronic configuration ( $[\text{Xe}] 4f^2 6s^2$ ), and presents two common valence states  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  [1–3], which give  $\text{CeO}_2$  excellent chemical and physical properties:  $1/4 \text{ O}_2$ , at most, can be released from each  $\text{CeO}_2$  unit cell. It serves as an active oxygen donor in many reactions, such as three-way catalytic reactions to eliminate toxic

automobile exhaust [1, 4], the low-temperature water gas shift reaction [1, 5], oxygen sensors, oxygen permeation membrane systems and fuel cells [1, 6]. Cerium oxide CeO<sub>2</sub> is a semiconductor oxide with a band gap energy (3.19 eV) [7, 8]. The crystalline structure consists of a cubic fluorite structure (Fm3m) with a cell parameter of 5.41 Å at room temperature and presents a high dielectric constant  $\epsilon = 26$ , almost of silicon, that it makes use in spintronic devices with silicon microelectronic devices [9, 10]. Synthesis of CeO<sub>2</sub> nanoparticles comprise various methods as: solvothermal [2, 11, 12], sol gel [2, 13, 14], sonochemical [2, 15], hydrolysis [2, 16], hydrothermal [2, 17, 18], precipitation [2, 19] and reverse micelles [2, 20]. The dual oxidation state mentioned above means that these nanoparticles have oxygen vacancies or defects [19]. The loss of oxygen and the reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> in accord with Eq. 1, is accompanied by creation of an oxygen vacancy. This property is responsible for the interesting redox chemistry exhibited by ceria nanoparticles and makes them attractive for many catalytic applications [21].



Also all ceria applications are based on its potential redox between Ce<sup>3+</sup> and Ce<sup>4+</sup>, high oxygen affinity and absorption/excitation energy bands associated with the electronic structure [22]. Another important property of CeO<sub>2</sub> consists in their ability to release and absorb oxygen during alternating redox conditions and hence to function as oxygen buffer. The addition of dopants leads to increase of concentration of oxygen vacancies and improves the thermal stability of the parent oxide [23]. Also, CeO<sub>2</sub> presents a great chemical stability and high diffusion coefficient with values between 10<sup>-8</sup> and 10<sup>-6</sup> cm<sup>2</sup>/s in the temperature range of 800–2200 K coming from oxygen vacancies (*V<sub>o</sub>* has been used for gas sensing for oxygen, NO<sub>x</sub>, acetone and H<sub>2</sub>S sensors). Besides, CeO<sub>2</sub> is also used for improving sensing properties of semiconductor oxides such as ZnO, TiO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> [24, 25]. On the other hand, the ionic conductivity of CeO<sub>2</sub> is improved by doping with rare earth oxides such as Sm<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> and the size of conductivity of the doped ceria depends on the ionic radius of the doping ion. The introduction of trivalent ions in ceria leads to production of anion vacancies

Sensitive material	Gas detected	Range concentration, [ppm]/[%]	Operation temperature, [°C]	Detection limit, [ppm]	Response/recovery time, [s]	Ref.
CeO <sub>2</sub> -SnO <sub>2</sub>	CO	0–500 ppm	430	<5	26/30	[27]
ZnO/Al <sub>2</sub> O <sub>3</sub> /CeO <sub>2</sub>	ethanol	0–2000 ppm	260	*	2/10	[28]
CeO <sub>2</sub> -Fe <sub>2</sub> O <sub>3</sub>	methanol	1–1000 ppm	400	1–3	*	[29]
CeO <sub>2</sub>	formaldehyde	0.5–50 ppm	30	—	36/1	[30]
CeO <sub>2</sub> activated ZnO-TiO <sub>2</sub>	CO <sub>2</sub>	286 ppm exposure	290	*	24/72	[31]
Ce <sub>(1-x)</sub> Zr <sub>x</sub> O <sub>2</sub>	O <sub>2</sub>	1–100%	500–700	*	*	[32]

\*Data unavailable.

Table 1. Gas detection with sensitive materials based on CeO<sub>2</sub>.

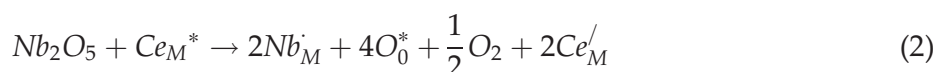
which may enhance catalytic and gas sensing properties [26]. In **Table 1**, several sensitive materials based on ceria for gas detection and their gas sensing characteristics is presented.

As doping with other ions could lead to enhanced activity for different reasons. Ceria doped with pentavalent ions as Nb, could insert extra oxygen anions that would be more easily removed [26]. In this chapter, the mixed oxides CeO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub>, Y<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub> as sensitive materials for CO<sub>2</sub> detection and sensitive materials composed from CeO<sub>2</sub>-doped rGO (reduced graphene oxide) and CeO<sub>2</sub>-doped rGO-ZnO for NO<sub>2</sub> detection are presented.

To conditioning the signal provided by sensing element, high-performance electronic circuits such as precision operational amplifiers, digital analogue converters and analog multipliers have been used [33, 34].

## 2. Sensor for CO<sub>2</sub> detection with mixed binary oxide CeO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub> sensitive material

Niobium oxide has some properties that make it in principal as promising for catalytic applications. Niobia-based materials are effective catalysts in selective oxidation reactions due to its redox properties. Also, niobia-doped ceria materials have shown a good carbon deposition and excellent properties as solid oxide fuel cell (SOFC) anodes [35]. Nb<sup>5+</sup> ions (ionic radius of Nb<sup>5+</sup>: 78 pm) may initiate the reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> by the doping Nb into the CeO<sub>2</sub> structure, which results in formation of oxygen vacancies. Using the Kröger-Vink notation, it can mention two mechanisms for the dissolution: one of which occurs by electronic compensation (Eq. 2) and the other by consumption of vacancies (Eq. 3), as shown below [3, 36, 37].



where O<sub>0</sub><sup>\*</sup>, V<sub>0</sub><sup>··</sup> represent oxygen and oxygen vacancies on the oxygen sites, Ce<sub>M</sub><sup>\*</sup>, Ce<sub>M</sub><sup>·/</sup> represent cerium (Ce<sup>4+</sup>) and negatively charged cerium ions (Ce<sup>3+</sup>) on metal sites M, Nb<sub>M</sub><sup>·</sup> metal vacancy. Nb<sub>2</sub>O<sub>5</sub> it is known as an n-type oxide semiconductor with a band gap about 3.4 eV. Because of its good physicochemical properties and structural isotropy, it is used in other range of applications such as: in construction of gas sensing, field-emission displays and microelectronics electrochromics display and photoelectrodes [38].

### 2.1. Synthesis of mixed oxides CeO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub> sensitive material

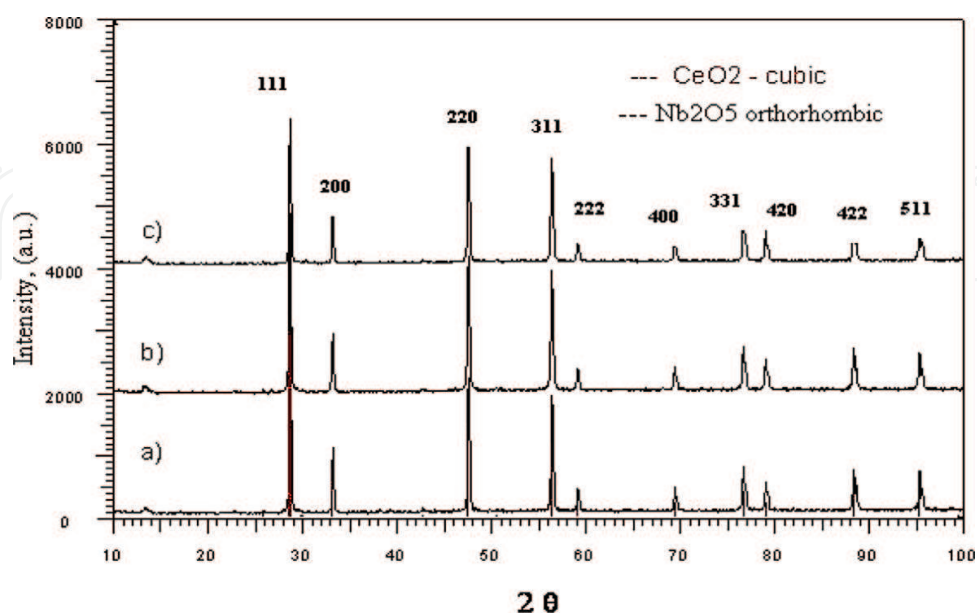
In our case, we used the mixed binary oxides CeO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub> for CO<sub>2</sub> detection. Sensitive element is composed from mechanical mixing of CeO<sub>2</sub> (97%) and Nb<sub>2</sub>O<sub>5</sub> (3%); both reagents purchased from Merck. The powder oxides were treated with a few drops of ethylic alcohol for ink obtaining and then introduced in a ball mill for homogenization followed by calcination at 500, 600 and 800°C for 1 hour. The powder calcined at 600°C was pressed in disc form at 2 tons force/cm<sup>2</sup> with the dimensions Ø4 × 1 mm and mounted on the ambasis transistor. The sensor image is showed in **Figure 1** [39].



**Figure 1.** Image of the CO<sub>2</sub> sensor made with mixed oxides CeO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub> sensitive material.

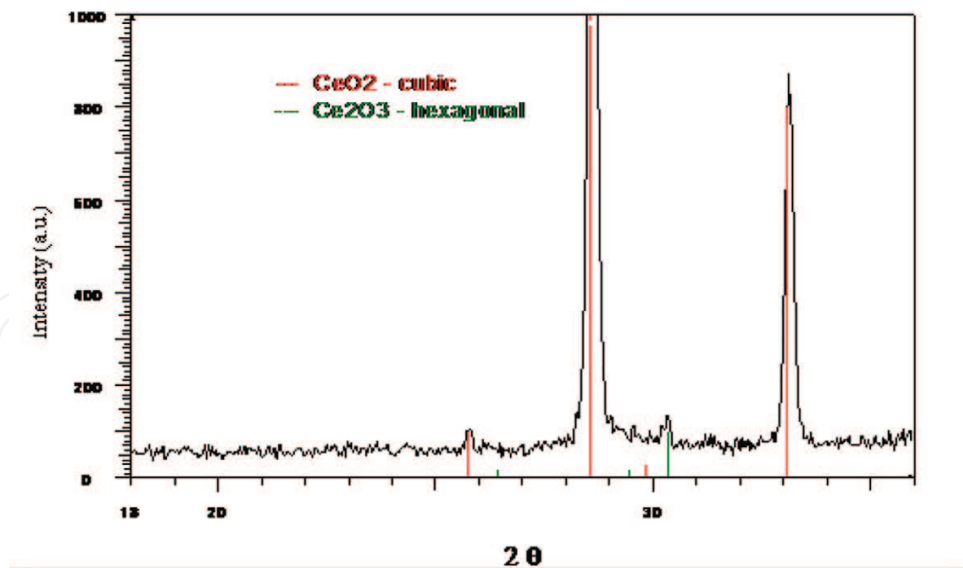
## 2.2. Structural characterization

Calcined mixed powder oxides were characterized by X-ray diffraction using a diffractometer-type X Bruker-AXS type D8 ADVANCE in conditions: CuK<sub>α</sub> radiation ( $\lambda = 1.54059 \text{ \AA}$ ), 40 kV/40 mA, filter k<sub>β</sub> of Ni. pas: 0.04°, measuring time on point: 1 s, measure range  $2\theta = 10\text{--}100^\circ$ . The mixed oxides powder with composition CeO<sub>2</sub>-3%Nb<sub>2</sub>O<sub>5</sub> was calcined at 500, 600 and 800°C for 1 hour. It shows a cubic phase for CeO<sub>2</sub> and orthorhombic phase for Nb<sub>2</sub>O<sub>5</sub>, **Figure 2**. Also, for this powder that was calcined at 800°C, was identified in addition a hexagonal Ce<sub>2</sub>O<sub>3</sub> phase (**Figure 3**). It obtain for CeO<sub>2</sub> cell parameter  $a = b = c = 5.407 \text{ \AA}$ . This is in accord with



**Figure 2.** X-ray diffraction of CeO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub> calcined at: (a) 500°C; (b) 600°C and (c) 800°C.





**Figure 3.** X-ray diffraction of  $\text{CeO}_2\text{-Nb}_2\text{O}_5$  calcinated at  $800^\circ\text{C}$ .

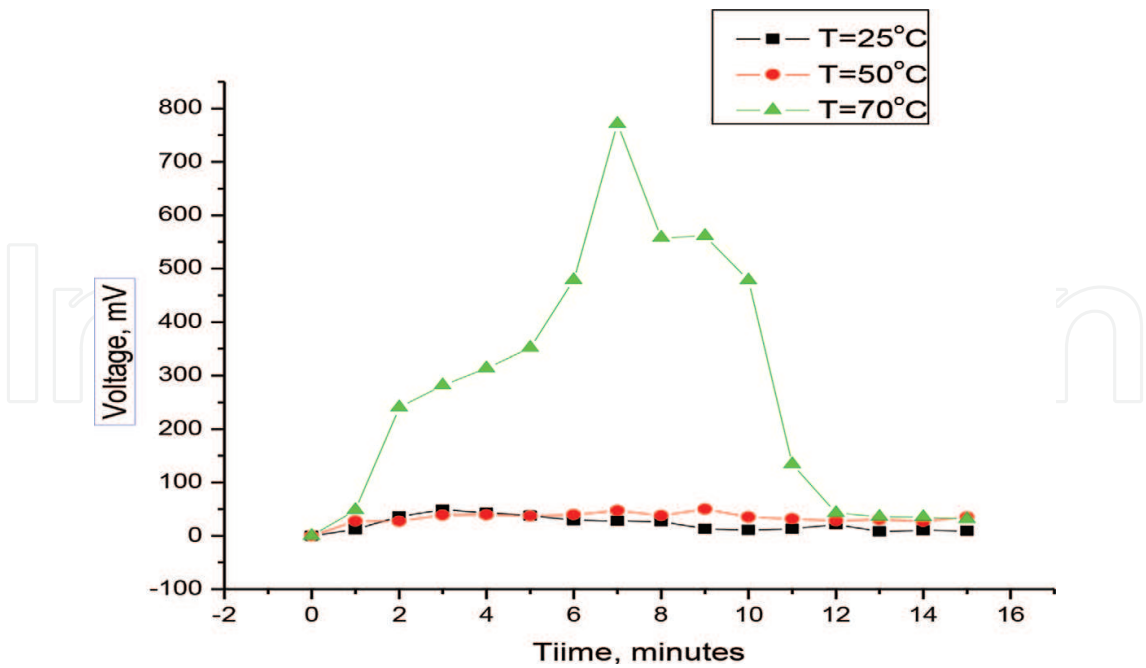
theoretical value of  $a = 5.404 \text{ \AA}$  as well as in according with card number 03-065-5923. The cell parameters for  $\text{Nb}_2\text{O}_5$  orthorhombic phase were  $a = 6.175 \text{ \AA}$ ,  $b = 29.175 \text{ \AA}$  and  $c = 3.930 \text{ \AA}$  in accord with card number 30-0873 [4]. Corresponding to hkl (Miller indices) 111, 200, 220 and 311, the crystallites size determined with Scherrer formula give values of 160.9, 145.6, 117.4 and 63.5 nm.

### 2.3. $\text{CO}_2$ gas sensor made with mixed oxides $\text{CeO}_2\text{-Nb}_2\text{O}_5$ sensitive material tested in automated process mode

The gas sensors testing were performed with the apparatus as presented in **Figure 4**. It is realized by SYSCOM-18 Romania for National Institute for Research and Development in



**Figure 4.** The testing gas sensor installation.



**Figure 5.** Variation of the voltage depending on time for CO<sub>2</sub> sensor, made with mixed oxides CeO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub> sensitive material.

Electrical Engineering ICPE-CA. The voltage measurements were effected by testing module, in automated process mode. A control panel provides a lot of measuring values, at rate 1/10 s. The bench of testing for the gas sensor consists in an enclosure where there are set of testing conditions for the sensor as well as in connected equipment. The whole process of testing is automated, being controlled by a programmable automaton. The gas for testing is introduced in a controlled way in the testing enclosure, through a mass debit meter. In the testing, enclosure is set a constant temperature, controlled by a temperature regulator.

The gas testing was done in concentration of 10,000 ppm CO<sub>2</sub> at the 25, 50 and 70°C chamber test temperature. The sensor was developed the voltages values of 48, 50 and 770 mV (**Figure 5**) [39].

The experimental data shows a good sensor response for CO<sub>2</sub> detection with increasing temperature.

#### 2.4. Signal conditioning of the sensing element for CO<sub>2</sub> detection with mixed binary oxide CeO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub> sensitive material

The Analog Devices AD620 operational amplifier is used to build the signal conditioning electronic module, provided by the sensing element. A preamp section comprised of Q1 and Q2, **Figure 6**, provides additional gain up front. Feedback through the Q1-A1-R1 loop and the Q2-A2-R2 loop maintains a constant collector current through the input devices Q1 and Q2, thereby impressing the input voltage across the external gain setting resistor, R<sub>G</sub>.

This creates a differential gain from the inputs to the A1/A2 outputs given by Eq. (4):

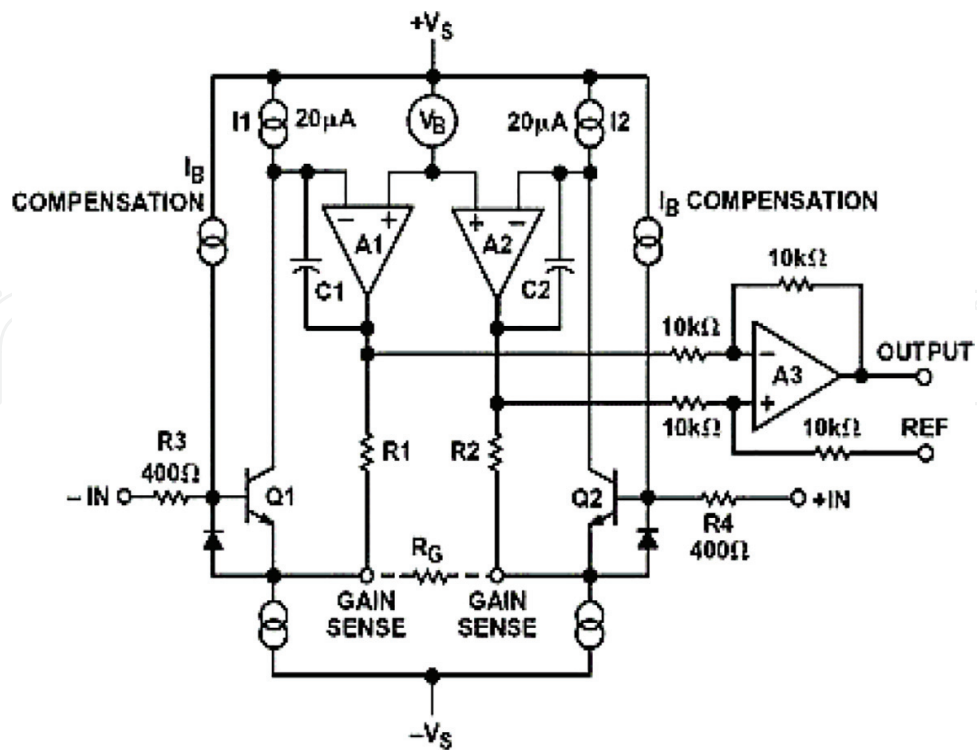


Figure 6. A simplified schematic of the AD620 [39].

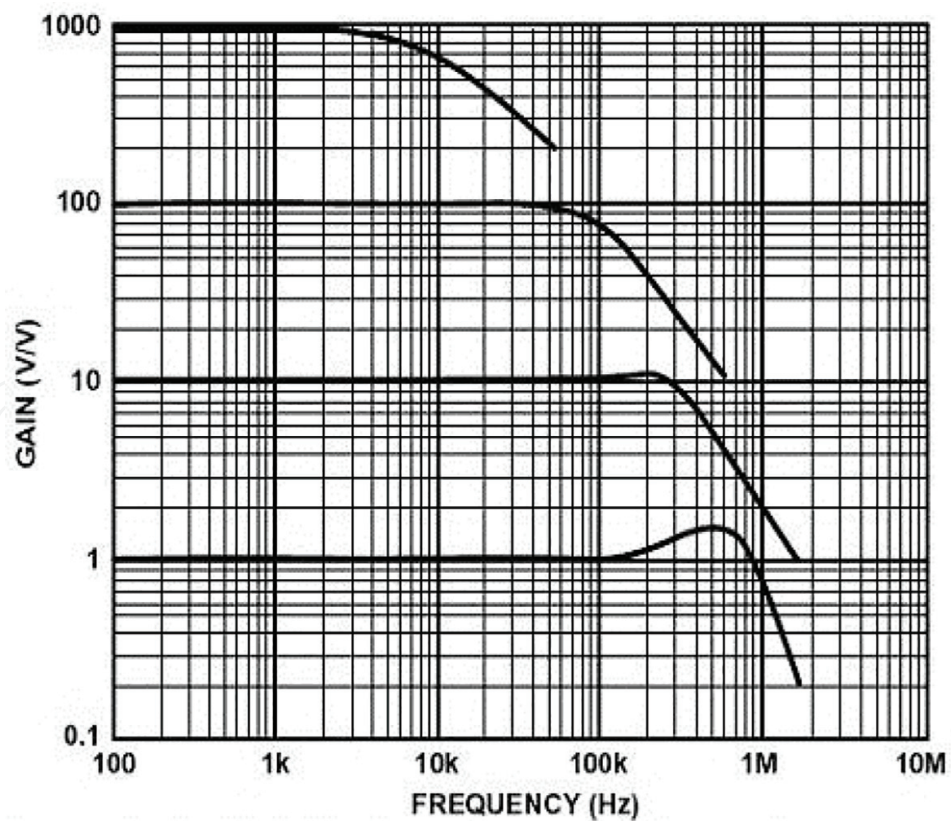
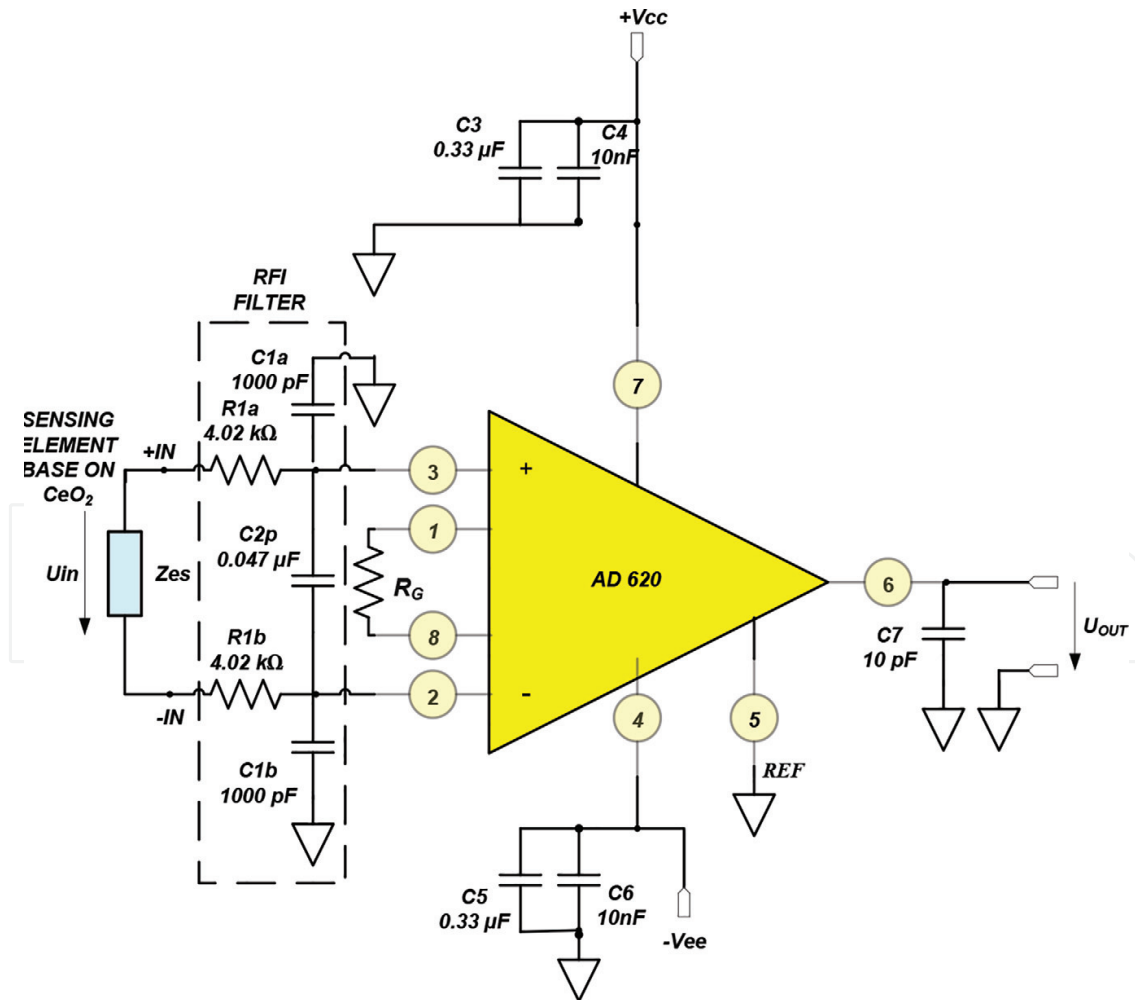


Figure 7. AD620 closed-loop gain versus frequency [39].



$$G = \frac{R1 + R2}{R_G} + 1 \quad (4)$$

The unity-gain subtractor, A3, removes any common-mode signal, yielding a single-ended output referred to the REF pin potential. The value of  $R_G$  also determines the transconductance of the preamp stage [34]. As  $R_G$  is reduced for larger gains, the transconductance increases asymptotically to that of the input transistors. The open-loop gain is boosted for increasing programmed gain, thus reducing gain related errors. Also, the gain bandwidth product (determined by C1, C2 and the preamplifier transconductance, **Figure 6**) increases with programmed gain, thus optimizing the amplifier's frequency response. In **Figure 7**, the closed-loop gain of AD620 versus frequency is shown. Finally, the input voltage noise is reduced to 9 nV/ $\sqrt{\text{Hz}}$ , which is determined mainly by the collector current and base resistance of the input devices. The internal gain resistors, R1 and R2, are laser trimmed to an absolute value of 24.7 k $\Omega$ , allowing the gain to be programmed accurately with a single external resistor. The gain equation is Eq. (5).



**Figure 8.** The electronic module for signal conditioning provided by sensing element, designing with AD620 analog devices.

$$G = \frac{49.4k\Omega}{R_G} + 1 \quad (5)$$

So that,

$$R_G = \frac{49.4k\Omega}{G - 1} \quad (6)$$

where the resistor  $R_G$  in k $\Omega$ , according to Eq. (6).

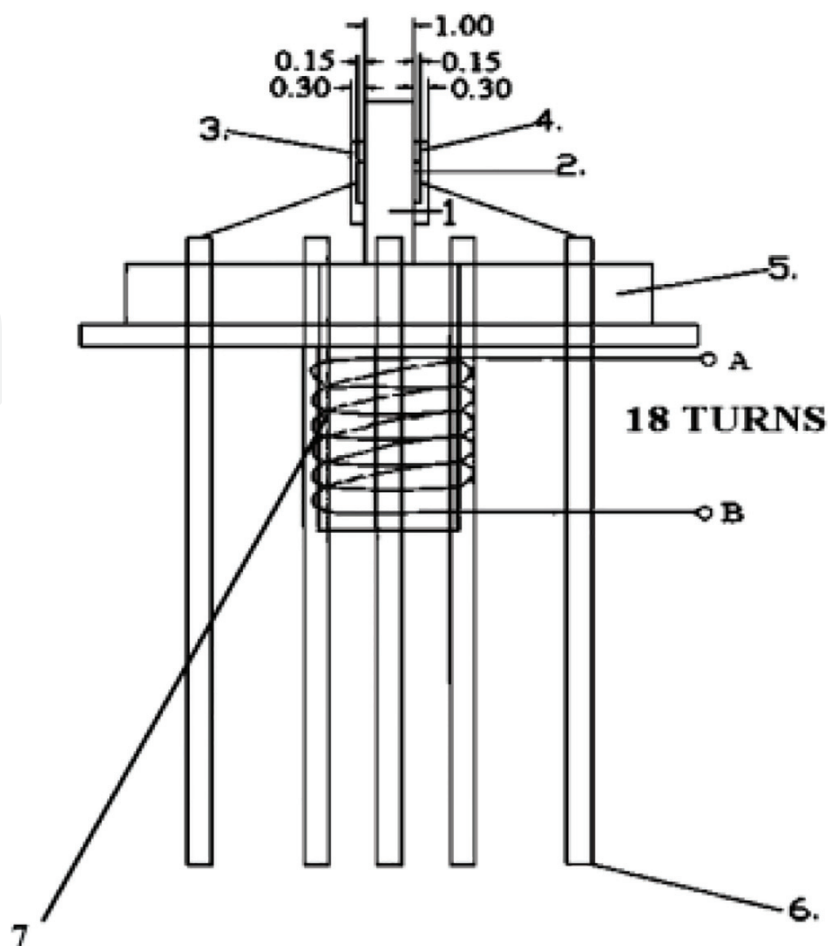
The value of 24.7 k $\Omega$  was chosen so that standard 1% resistor values could be used to set the most popular gains. For the input resistors,  $R_{1a}$  and  $R_{1b}$  were used, capacitor C2p approximately five times to 0.047  $\mu$ F to provide adequate RF attenuation (**Figure 8**). With the values shown, the circuit –3 dB bandwidth is approximately 400 Hz and noise levels 12 nV/ $\sqrt{\text{Hz}}$ . It requires the circuitry preceding the in-amp to drive a lower impedance load and results in somewhat less input overload protection. The output signal  $V_{\text{OUT}}$  (**Figure 8**) is a common mode voltage, picked at the output of the operational amplifier. The capacitor groups, 0.01  $\mu$ F and 0.33  $\mu$ F make a decoupling of the supply voltage (**Figure 8**) in the immediate closeness of the operational amplifiers. The supply voltage + $V_{\text{cc}}$  and - $V_{\text{ee}}$ , respectively, stabilized is differentiated,  $\pm 15V_{\text{cc}}$ , in comparison with the reference potential bar.

### 3. Sensor for CO<sub>2</sub> detection with Y<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub> sensitive material

The ion conductivity of CeO<sub>2</sub> can be significantly improved upon substitution with some trivalent oxides of lanthanides like Y<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub> and Gd<sub>2</sub>O<sub>3</sub>, because the number of oxygen vacancy will be considerably increased for charge compensation. The electrical conductivity in doped ceria is influenced by factors such as: the dopant ion, the dopant concentration, the oxygen vacancy concentration and the defect association enthalpy. An example is constituted by combination Y<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub> which has been used usually as the solid electrolyte for moderate temperature solid oxide fuel cells [40]. In our case, we used the Y<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub> as sensitive material for CO<sub>2</sub> detection. For Y<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> synthesis, it utilizes several methods such as hydrothermal [41], electrospinning [23], thermolysis [42] and sol gel [43].

#### 3.1. Synthesis method

Sol gel method applied for synthesis of Y<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub> sensitive material, is in accord with ref. [44] and used as starting reagents Ce(SO<sub>4</sub>)<sub>2</sub> × 4H<sub>2</sub>O (97% purity, Merck) and Y(NO<sub>3</sub>)<sub>3</sub> × 3H<sub>2</sub>O (98% purity Karlsruhe GmbH in molar ratio CeO<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> = 4:1). The salts were dissolved in deionized water. To 100 ml salt solution, 25 ml solution of 1 M citric acid as chelating agent was added. To obtain gel, the salt solution was heated to 70°C under constant stirring. To this solution, 40 ml ethylene glycol was added to promote citrate polymerization and heated at 90°C. The gel formed was filtered, washed and heat treated in oven at 100°C. The powder obtained was calcined at 800°C for 2 hours. The powder was pressed to disc form using 10 ton force/cm<sup>2</sup>, with dimensions diameter 4 mm, height 1 mm and then sinterized at 1100°C for 6 hours [44].



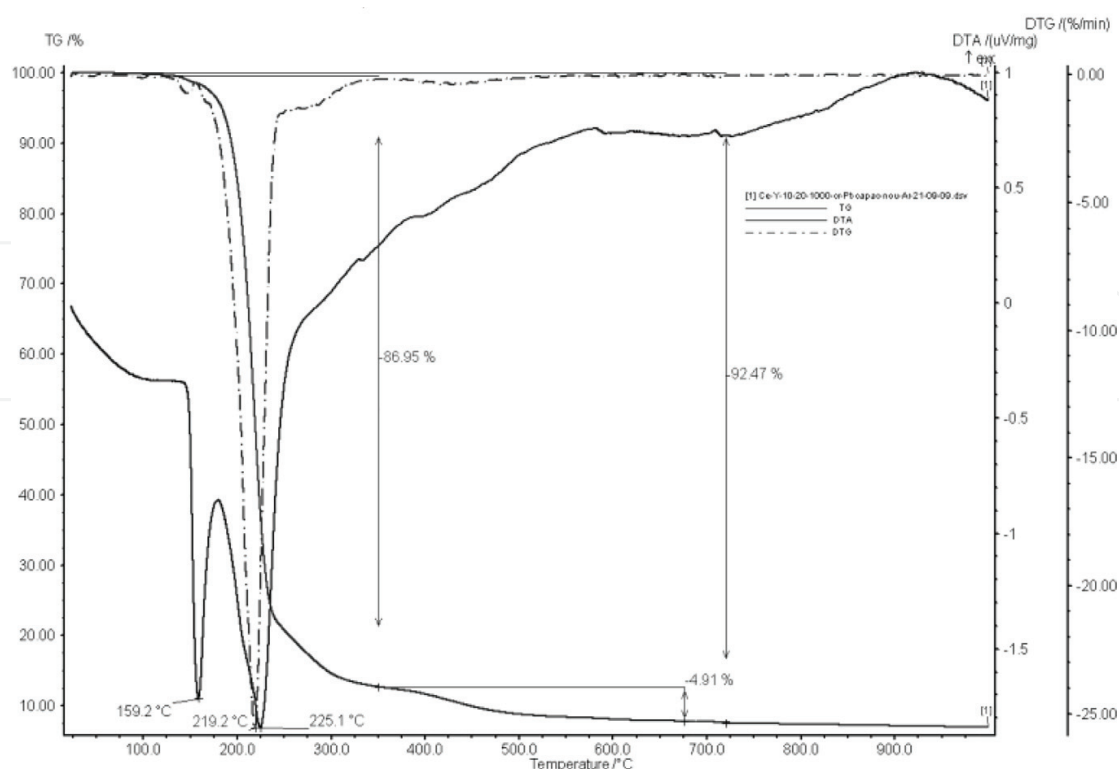
**Figure 9.** CO<sub>2</sub> sensor, component parts: 1. Ce<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub> disc; 2. Gold electrode, thin film deposition of Au, in the form of the disc; 3. Ag micro-wire connections; 4. The positioning piece; 5. TO-8 package plated base; 6. The pins; 7. A, B terminals of 18 turns heating resistance.

### 3.2. The construction of the sensor for CO<sub>2</sub> detection designed with Y<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub> sensitive material

On both sides of disc, gold electrodes in circular form with diameter of 1 mm was deposited. The gold was deposited by e-beam evaporation method using Baltzer equipment with conditions: pressure  $P = 10^{-5}$  Torr and current  $I = 8$  mA, for 60 s time deposition. The disc with electrodes deposited was mounted on a 12 pin TO-8 package base. Below the base, the heater element composed of Ni wire with a diameter of 0.1 mm was placed, the winding is composed from 18 turns with a diameter of  $d = 3$  mm. **Figure 9** shows how it built the CO<sub>2</sub> sensor [44].

### 3.3. Structural and morphological characterization of sensitive material Y<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub>

Thermal analysis was performed with NETZSCH STA 409 simultaneous thermogravimetric balance, in the analysis conditions: inert atmosphere of argon, heating rate of 10°C/min in alumina crucible and the mass sample was 15.7 mg. **Figure 10** presents the thermal analysis TG, DTA and differential thermogravimetry (DTG) curves for the dried gel. The DTA curve



**Figure 10.** Thermal analysis TG, DTA and DTG curves for dried gel of CeO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>.

releases two endothermic peaks at 159.2 and 225.1°C. The last one has a correspondent in DTG curve at 219°C, the total mass loss was 86.95% from initial mass. Other thermal transformation appears at 430°C which represents on in a TG curve a loss of 4.91% which correspond to the decomposition of precursors, consisting in cerium sulfate and yttrium nitrate and in the end only Ce-Y-related oxides are obtained [44].

The X-ray diffraction patterns of the CeO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> oxides powder calcinations at 800°C for 2 hours are shown in **Figure 11**. For comparison, **Figure 12** shows the X-ray diffraction for commercial CeO<sub>2</sub> powder. For this oxides system, the XRD pattern reveals the formation of well crystallized phases, CeO<sub>2</sub> indexed with the cubic fluorite structure and Y<sub>2</sub>O<sub>3</sub> with cubic structure. Also, a secondary phase with cubic structure and composition Ce<sub>0.6</sub>Y<sub>0.4</sub>O<sub>1.8</sub> was identified [44].

**Table 2** presents X-ray parameters for Y<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub>, cell parameters and crystallite sizes determined with Scherrer formula.

The morphological structure of Y<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub> was investigate by SEM measurements using FESEM-FIB type Auriger model Carl Zeiss SMT GmbH at a high voltage acceleration of 2 and 3 kV. The SEM sample morphology was investigated trough SESI (combined detector in SEM chamber–Evernhart Thornley type with Faraday cup). **Figure 13** shows the SEM image for disc CeO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> sintered, where it can be seen as a relative homogeneous structure and the crystallite sizes of CeO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub> were in range of 26–54 nm in good accord with X-ray diffraction analysis. **Figure 14** shows the SEM images for CeO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> powder calcined at

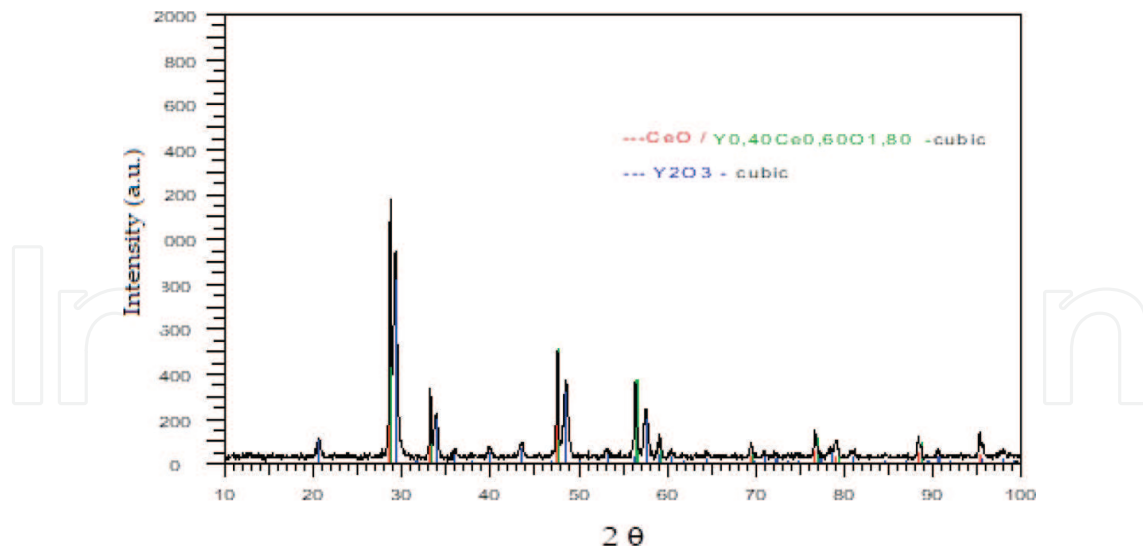


Figure 11. X-ray diffraction of Y<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub> synthesized by sol gel method.

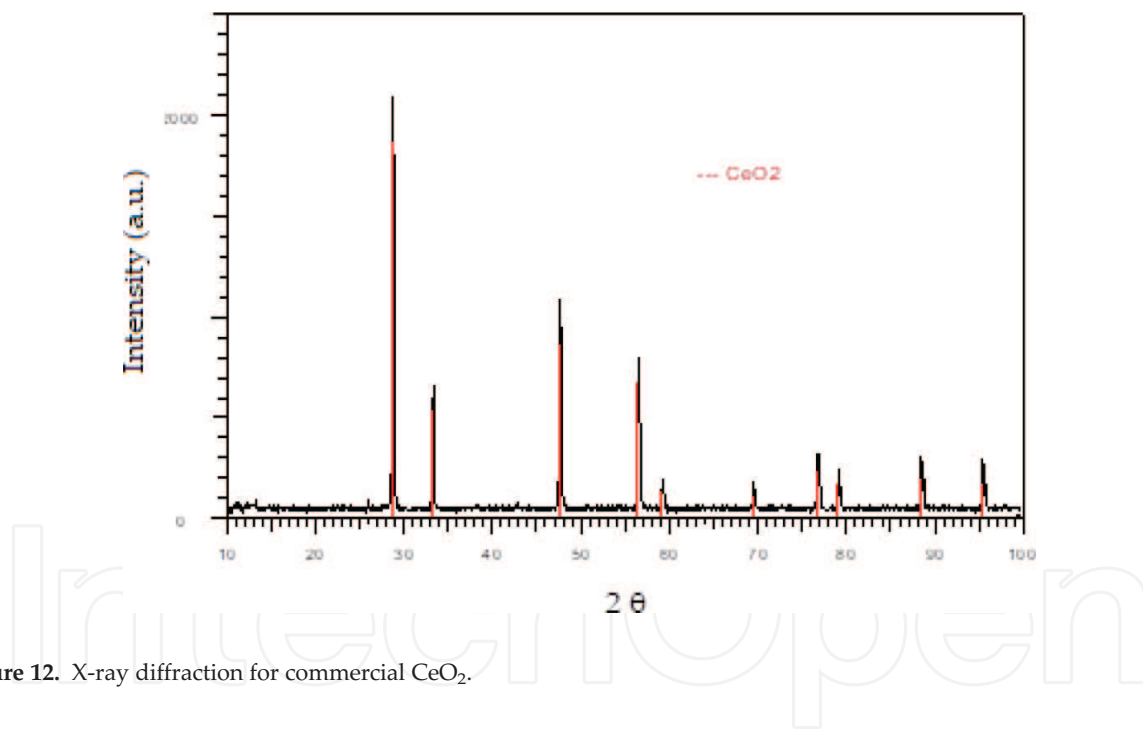


Figure 12. X-ray diffraction for commercial CeO<sub>2</sub>.

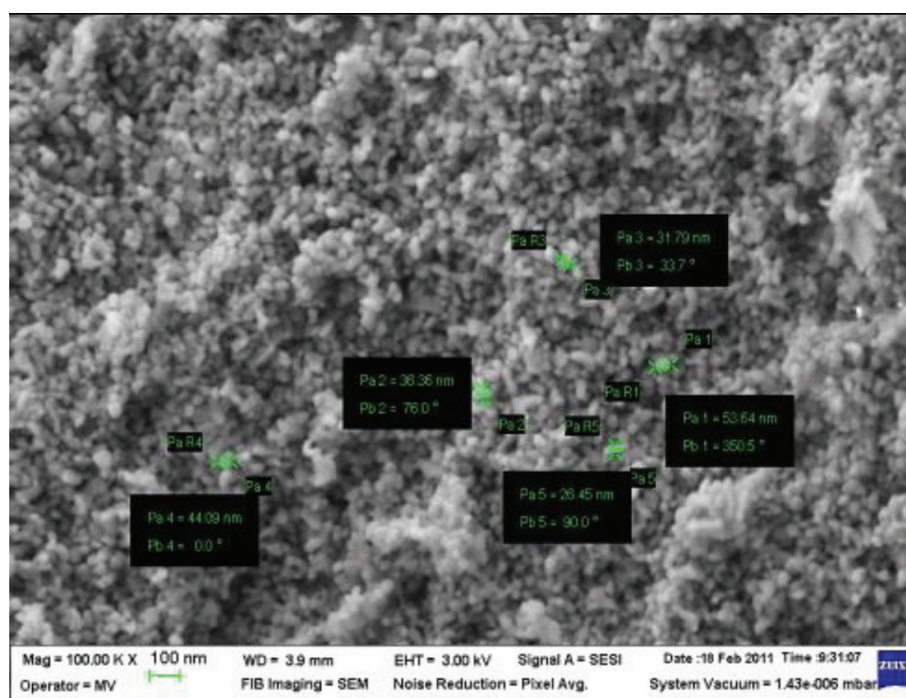
800°C for 2 hours, where it can be see a nonhomogeneous structure composed by agglomerates [44].

N<sub>2</sub> adsorption desorption isotherms were performed with the AUTOSORB-1, Quantachrome Instruments, United Kingdom in the following conditions: working gas N<sub>2</sub>, measured temperature: −196°C and relative pressure range  $P/P_o = 0.001\text{--}0.99$ . For binary oxides CeO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>, powder calcined at 800°C for 2 hours, BET analysis revealed the results: the specific surface area was 3.13 m<sup>2</sup>/g, the total volume of the pores was 1.066x10<sup>−3</sup> cm<sup>3</sup>/g and pore sizes of 8.93 Å. There is a specific ratio  $P/P_o = 0.02898$  for the pores with diameters smaller than 6.9 Å [44].



Phase	Crystal structure	Unit cell parameter (Å) a = b = c		2θ	Crystalline face indexes hkl	Crystallites-size (nm)
		Experimental	Theoretic card no.:			
CeO <sub>2</sub>	Cubic	5.41325	5.41100 PDF 01-071-4199	28.536	111	48.1
Y <sub>2</sub> O <sub>3</sub>	Cubic	10.61131	10.61060 PDF 01-076-8044	29.121	222	27.0
Y <sub>0.4</sub> Ce <sub>0.6</sub> O <sub>1.8</sub>	Cubic	5.39449	5.39300 PDF 01-075-0177	28.639	111	49.2
CeO <sub>2</sub> Merck	Cubic	5.384			111	154.9

**Table 2.** X-ray parameters for Y<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub>.



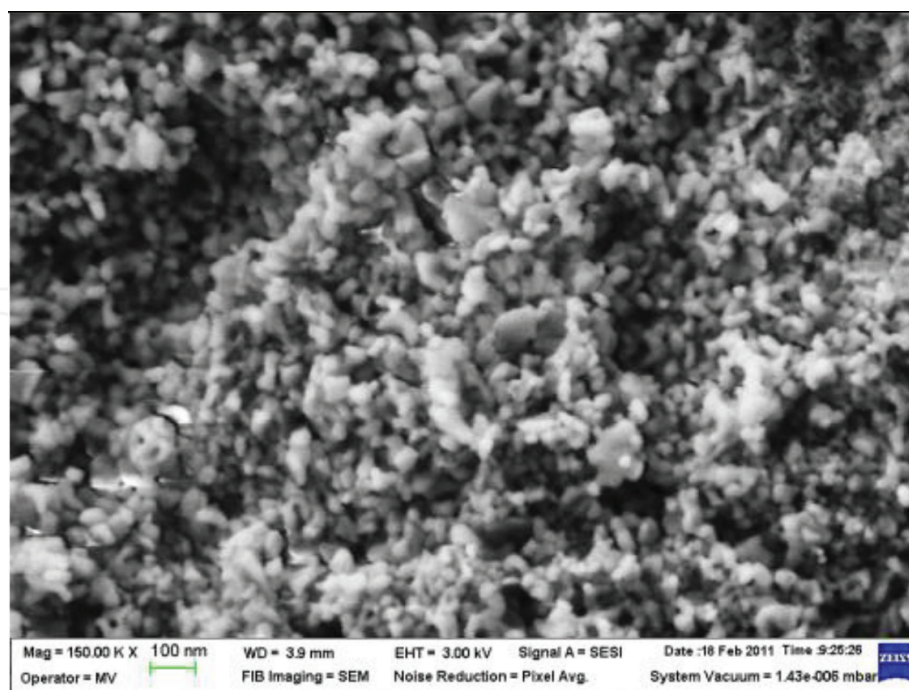
**Figure 13.** SEM images for sintering disc CeO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>.

### 3.4. The CO<sub>2</sub> gas sensing mechanism and gas sensors testing

The improved sensing response at CO<sub>2</sub> can be attributed to synergistic effects between Y<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub>. In certain conditions such as high temperature, reduced state or pure CeO<sub>2</sub>, lose some amount of oxygen and generate oxygen vacancies in accord with Eq. (7),



When CO<sub>2</sub> comes in contact with CeO<sub>2</sub>-activated surface, this forms carbonates as a product through the participation of surface oxide ions in accordance with Eq. (8),



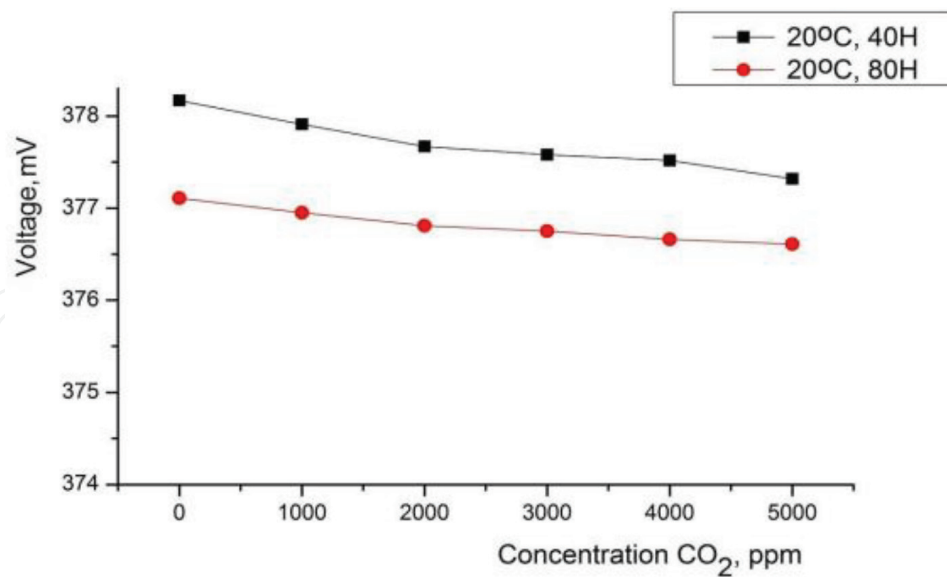
**Figure 14.** SEM images for oxidic powder  $\text{CeO}_2\text{-Y}_2\text{O}_3$  calcined at  $800^\circ\text{C}$  for 2 hours.



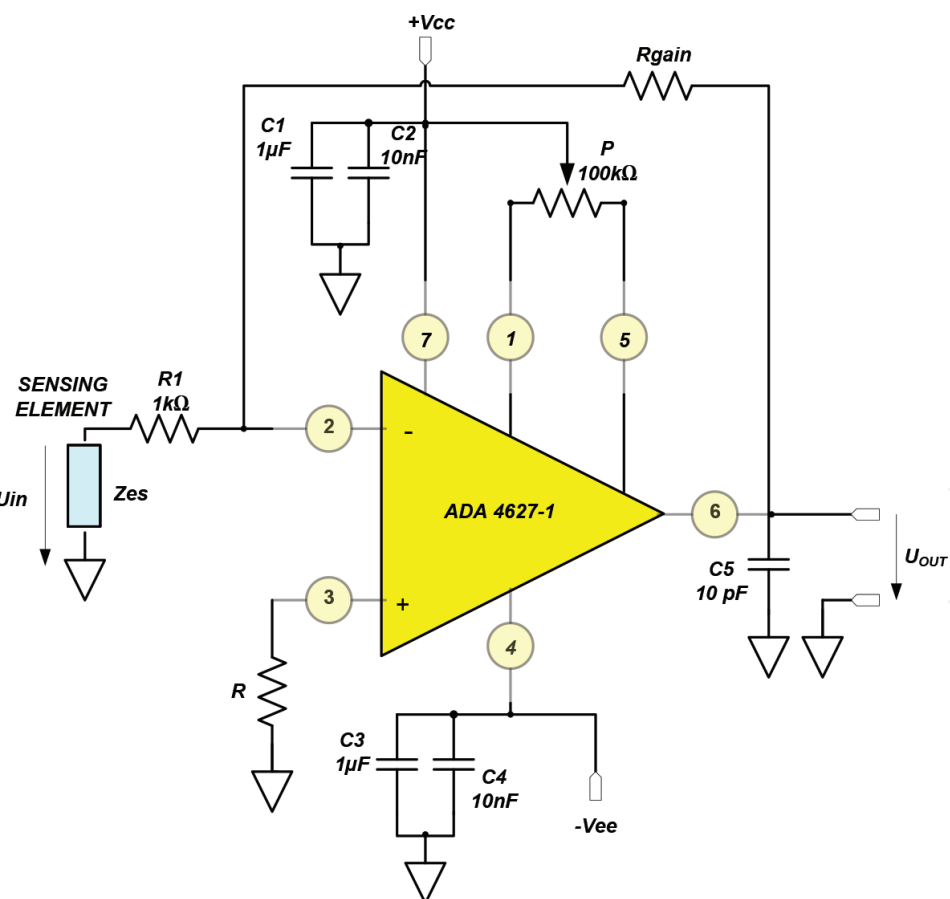
The carbonates disappear when they are exposed to oxidizing conditions [31]. The sensor characteristic was performed using test installation presented in **Figure 4**. The sensor was exposed at  $\text{CO}_2$  atmospheres in the concentration range of 0–5000 ppm  $\text{CO}_2$  in the climatic conditions:  $T = 20^\circ\text{C}$  and two relative humidity testing 40% RH and 80% RH, respectively. The sensor functions at  $135^\circ\text{C}$ , temperature provided by the heating resistance (**Figure 9**, Pos. 7). **Figure 15** shows the variation of sensor voltage with the gas concentration. The characteristics show a slow linear decreasing of voltage with  $\text{CO}_2$  concentration which allows an easy signal conditioning. In the concentration range 0–5000 ppm  $\text{CO}_2$ , the sensor presents a voltage variation as follows: 378.17–377.32 mV for  $T = 20^\circ\text{C}$ , RH 40% and 377.11–376.61 mV for  $T = 20^\circ\text{C}$ , RH 80%. The sensor data show a little dependence of voltage with relative humidity that makes usable in environment with high relative humidity. The sensitivity of the sensor was 0.3 V/ppm and the response time was less than 30 s [44].

### 3.5. Signal conditioning of the sensing element for $\text{CO}_2$ gas detection with $\text{Y}_2\text{O}_3$ -doped $\text{CeO}_2$ sensitive material

The operational amplifier ADA4627-1, provided by analog devices (**Figure 16**) is a broadband and high precision amplifier. It is recommended in applications like “sensor conditioning” and electronic conditioning of the signal, due to its exceptional attributes: low noise, very low offset voltage, very high common-mode rejection ratio (CMMR) and very high slew rate. This operational amplifier combines the best “DC” features and very good dynamic characteristics



**Figure 15.** The sensor voltage function with  $\text{CO}_2$  concentration, for  $T = 20^\circ\text{C}$  and two relative humidity testing 40% RH and 80% RH, respectively.



**Figure 16.** The electronic module for signal conditioning provided by sensing element, designing with ADA4627-1 analog devices.

[33], like: slew rate 60 V/ $\mu$ s; extended range of differential supply voltage:  $\pm 5$  Vcc ....  $\pm 15$  Vcc; opn loop gain 120 dB; low offset voltage maximum 200  $\mu$ V and the bias current: maximum 5 pA.

## 4. NO<sub>2</sub> gas sensor made with rGO-doped CeO<sub>2</sub> and CeO<sub>2</sub>-doped rGO/ZnO

### 4.1. Synthesis of sensitive materials rGO-doped CeO<sub>2</sub> and CeO<sub>2</sub>/rGO-doped ZnO

In order to study the CeO<sub>2</sub> sensor properties for NO<sub>2</sub> detection, two sets of sensitive materials for sensors was synthesized: (a) 1%rGO/CeO<sub>2</sub> nanocomposite as sensitive material to study the effect of rGO adding on the sensitivity and (b) 1%(wt. %)CeO<sub>2</sub> was added at 1%(wt.%) rGO/ZnO-nanocomposite, in order to study the effect of CeO<sub>2</sub> adding on the sensitivity.

- A. Synthesis of 1%rGO/CeO<sub>2</sub>: 1%(wt.%) rGO/CeO<sub>2</sub> nanocomposite was synthesized in situ by precipitation method using Ce(NO<sub>3</sub>)<sub>3</sub> and NH<sub>3</sub> (25% conc) at 90°C and 30 min maturation time.
- B. Synthesis of 1%CeO<sub>2</sub>/1%rGO/ZnO: The 1%(wt.%)GO and 1%CeO<sub>2</sub> was mixed with ZnO in ethanol. The resulted powder after ethanol evaporation was heat treated at 150°C. The GO was synthesized by Hummers' modified method using as strong oxidant potassium permanganate (mass ratio C:oxidant = 1:3) in a solution of sodium nitrate and concentrated sulfuric acid (1 g/150 ml) and graphite [45, 46].

### 4.2. Structural and morphological characterizations of the sensitive materials

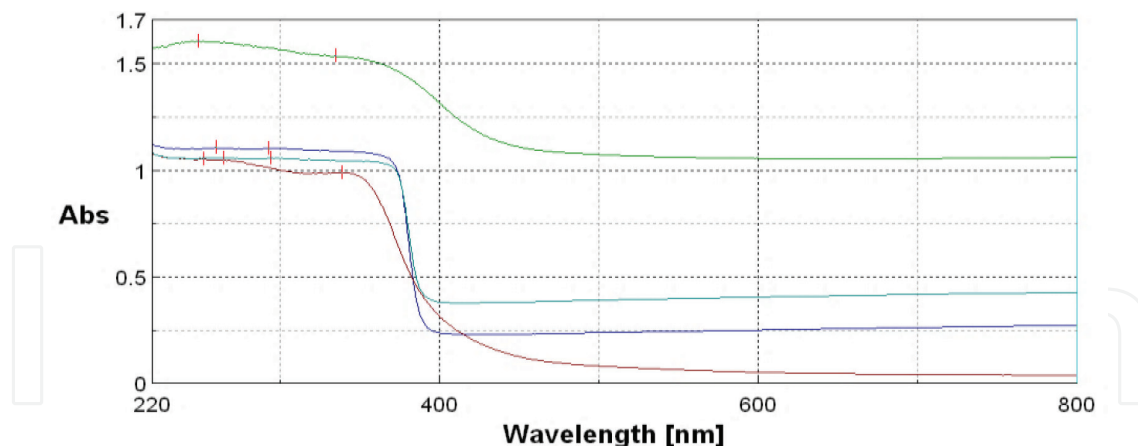
UV-Vis diffuse reflectance spectroscopy measurements were performed a Jasco V-570 Spectrophotometer, Japan, equipped with integrating sphere for diffuse reflectance measurement mode and SPECTRALON reference as etalon, and bang gap software in order to evaluate the optical properties and band gap values of the CeO<sub>2</sub>, doped CeO<sub>2</sub> with 1%rGO and doped 1%GO-ZnO nanocomposite with 1%CeO<sub>2</sub>. The diffuse reflectance spectrum was converted in absorbance spectrum and presented in **Figure 17**. The band gap was calculated using Kubelka-Munk equation with associated plot  $\sqrt{\alpha h\nu}$  versus photon energy  $E_g$  [eV], where  $\alpha$  is extinction coefficient [ $\text{cm}^{-1}$ ] and  $h$  is Planch constant  $4.135 \times 10^{-15}$  [eVs],  $\nu$  is light frequency [ $\text{s}^{-1}$ ] and wavelength [nm] [47–49]. The linearity coefficient was in all case bigger than 0.99.

In **Table 3**, the UV-Vis spectra parameters of UV-Vis measurements, for 1%rGO/CeO<sub>2</sub> and CeO<sub>2</sub> is also presented.

Legend:  $A_{\text{abs}}$  represents absorbance plasmon resonance (APR) and  $I$  represents intensity of APR.

The effect of doping of CeO<sub>2</sub> with 1%rGO leads to blue shift of APR presented in **Table 3** and **Figure 17** accompanied by the hyperchromic effect for both peaks, while the band gap are narrows, keeping the same characteristic shape of the ceria spectrum. The same effect—a blue shift has been described in literature for both TiO<sub>2</sub> aditived with GO and for ZnO aditived with





**Figure 17.** Diffuse reflectance UV-Vis spectroscopy spectra for CeO<sub>2</sub> (red), (1%CeO<sub>2</sub>/1%rGO) ZnO (blue), 1%rGO/ZnO (cyan) and 1%rGO/CeO<sub>2</sub> (green).

Samples	Abs <sub>max1</sub>	I1	Abs <sub>max2</sub>	I2	Band gap, [eV]	
1%rGO/CeO <sub>2</sub>	249	1.065	335	1.535	3.05	
	Blue shift	Hyper chromic effect	Blue shift	Hyper chromic effect	band gap narrowing	
CeO <sub>2</sub> -standard	252	1.051	339	0.99	theoretical	Commercial type
					3.19, Ref. [47]	3.16

**Table 3.** UV-Vis spectra parameters of UV-Vis measurements.

GO [50, 51]. The introduction of 1%GO(wt.%) in CeO<sub>2</sub> leads to a decrease in the effective optical band gap value from 3.16 eV to 3.05 eV, with a variation of 0.11 eV. This shows that the 1%GO(wt.%) acted as a band gap modifier [47–49, 52]. The same effect has been described in literature for the introduction of GO and related materials rGO in TiO<sub>2</sub> leads to a decrease in band gap [50]. Earlier, a lot of researchers attempt to tailor the properties of oxide semiconductors by using band gap modifiers and in this way to improve the catalytic, photovoltaic and sensing properties; this new trend is named bend gap engineering [47–49, 52]. Many researchers obtained a band gap narrowing after heat treatment of CeO<sub>2</sub> [52] and doping with different metals as Co [52], Gd [53], functionalized by different techniques [47], etc. Rare earth oxides present a high basicity related to ordinary oxide semiconductors such as TiO<sub>2</sub>, WO<sub>3</sub>, SnO<sub>2</sub> and ZnO, fast oxygen ion mobility and interesting catalytic properties which are important in gas sensing application [54–56]. **Table 4** presents UV-Vis spectra parameters of UV-Vis measurements for 1%CeO<sub>2</sub>/1%rGO/ZnO and 1%rGO/ZnO.

In the case of doping with 1%(wt.%)CeO<sub>2</sub> of the 1%(wt.%)rGO/ZnO nanocomposite, the effect is the same, an increasing of APR accompanied by the hyperchromic effect with the preservation of the characteristic spectra shape. But in opposite with the first case of CeO<sub>2</sub> doped with 1%GO(wt. %), there is a decrease in effective optical band gap value from 3.24 to 3.19 eV, with a variation of 0.05 eV. This shows that the 1%CeO<sub>2</sub>(wt.%) acted as a band gap modifier. The UV-Vis spectra present a strong absorption bands below 400 nm in UV region for the nanocomposites with the main component ZnO which are attributed to ZnO NP. The APR of ZnO nanocomposites are

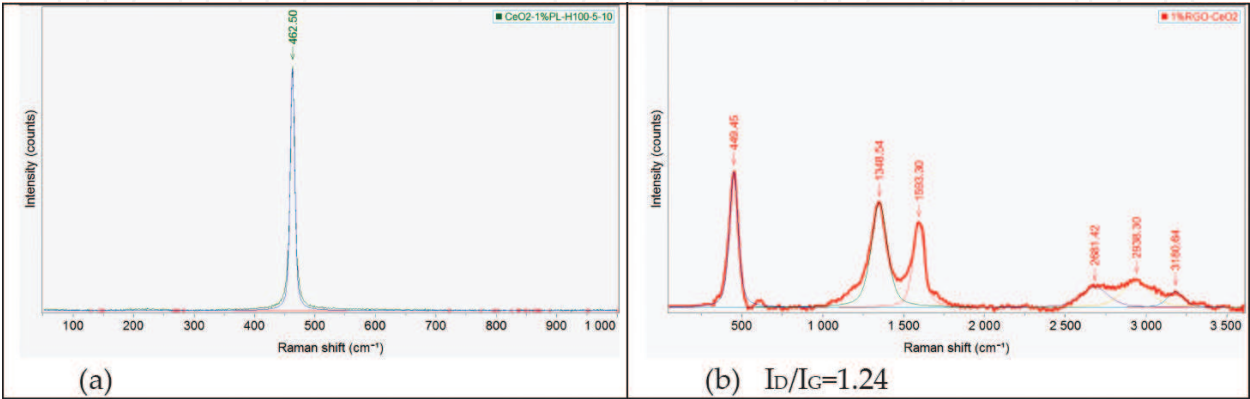


Samples	Abs <sub>max</sub> 1	I1	Abs <sub>max</sub> 2	I2	Band gap, [eV]
1%CeO <sub>2</sub> /1%rGO-ZnO	260	1.104	293	1.103	3.19
	Blue shift	Hyper chromic effect	Blue shift	Hyper chromic effect	Band gap narrowing
1%rGO-ZnO-etalon	265	1.059	294	1.056	3.25
ZnO	376	—	—	—	Theoretic
	Ref. [60]				3.37
					Ref.: [48], [57–60]

Legend: A<sub>abs</sub> represents absorbance plasmon resonance (APR) and I represents intensity of APR.

**Table 4.** UV-Vis spectra parameters of UV-Vis measurements for 1% CeO<sub>2</sub>/1%rGO/ZnO and 1%rGO/ZnO.

lower, in generally, than the absorption band of bulk ZnO (373 nm) that had a wide direct band gap at room temperature of 3.37 eV [48, 57–60]. CeO<sub>2</sub> adding on ZnO nanocomposite surface leads to a significant increase of the absorption in the UV light spectrum and decrease in the visible light spectrum. Based on the above results, UV-Vis and transformed Kubelka–Munk function plots suggested that are necessary energy for generation of electrons in conduction bands and holes in valence bands is smaller for the doped 1%rGO/CeO<sub>2</sub> than the CeO<sub>2</sub>, this makes the doped CeO<sub>2</sub> more reactive and sensitive. Other researchers tried to improve the sensing properties of ZnO sensor, for ethanol detection, by adding noble metals such as Pd [61], Pt [62] and Au [63], other metals such as Al, In, Cu, Fe and Sn [64], oxides as TiO<sub>2</sub> [65], CuO [66], CoO [67], RuO<sub>2</sub> [68] and SnO<sub>2</sub> and not in the end Ce and CeO<sub>2</sub> [55]. There is a current practice to use band gap modifiers. Many researchers use a band gap modifier in order to improve the functional properties of nanocomposite based on semiconductors oxides. The functional properties are ranging from the photocatalytic properties, sensitivity and selectivity for different sensor types, catalysts and others [52]. Raman spectroscopy measurements was performed with Raman dispersive spectrometry–LabRam HR Evolution, Horiba Jobin Yvone, France, equipped with Laser wave 532 nm, acquisition time 5 s, 10 accumulation, 0.1% laser power, used in order characterized the order-disorder degree in the synthetized nanocomposite. **Figure 18** shows the RAMAN spectra for CeO<sub>2</sub> and rGO/CeO<sub>2</sub>.

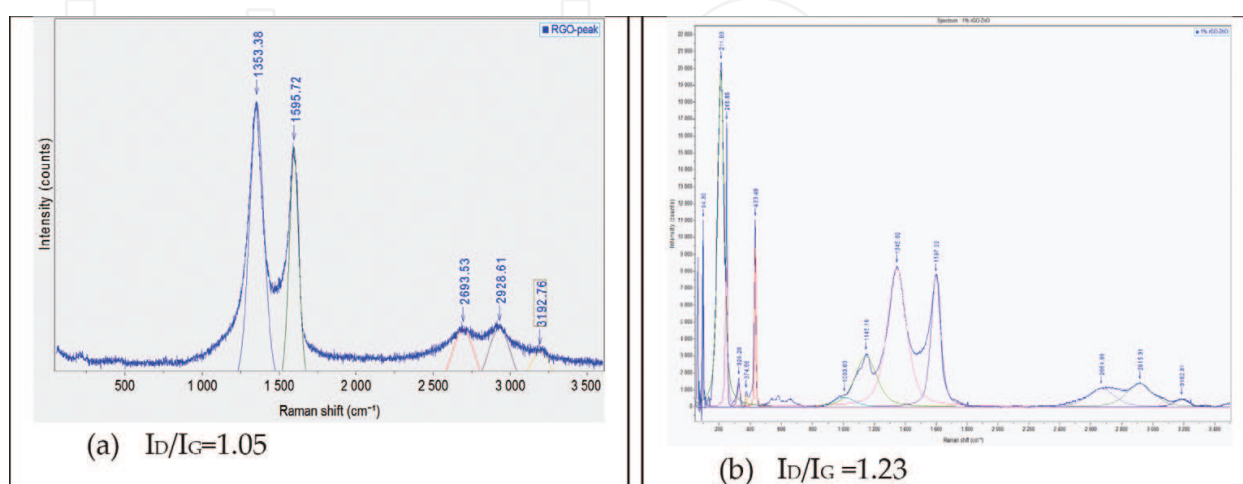


**Figure 18.** Raman spectra for CeO<sub>2</sub> powder (a) and synthesized 1%rGO/CeO<sub>2</sub> (b).

**Figure 18(a)** presents the Raman spectrum of CeO<sub>2</sub> powder which reveals a peak situated at 462.5 cm<sup>-1</sup> characteristic for CeO<sub>2</sub>, corresponding to the Raman active modes F<sub>2g</sub> for Ce–O symmetric breathing mode of oxygen atoms around the Ce atoms [49]. **Figure 18(b)** shows the Raman spectrum of 1%rGO/CeO<sub>2</sub> with characteristic peak of ceria at 449 cm<sup>-1</sup> corresponding to the Raman active modes of CeO<sub>2</sub> and characteristics graphene oxide peaks [69] at 1348.54 cm<sup>-1</sup> (D band), 1593.30 cm<sup>-1</sup> (G band), 2681.42 cm<sup>-1</sup> (2D band), 2938.30 cm<sup>-1</sup> (2D + D' band) and 3180.64 cm<sup>-1</sup> (G + D' band). According to the Raman line, broadening is equivalent with lattice constant cell crystallographic parameter a<sub>0</sub> of CeO<sub>2</sub> can be estimated by Eq. (9) [49], with 0.9 nm for CeO<sub>2</sub> powder and 0.43 nm for the CeO<sub>2</sub> from the 1% rGO-CeO<sub>2</sub> nanocomposite. The characteristic peak of CeO<sub>2</sub> was shifted with 13.05 cm<sup>-1</sup> at lower wave number as a doping effect of 1%rGO.

$$FW[cm^{-1}] = 10 + \frac{124,7}{d} [nm] \quad (9)$$

where the FW is full wide at half-maximum of the Raman active mode F<sub>2g</sub> and d is the diameter particle in nm. **Figure 19(a)** shows the Raman spectrum of GO with characteristic peaks of graphene oxide peaks at 1347.96 cm<sup>-1</sup> (D band), 1595.33 cm<sup>-1</sup> (G band), 2681.77 cm<sup>-1</sup> (2D band), 2914.68 cm<sup>-1</sup> (2D + D' band) and 3196.75 cm<sup>-1</sup> (G + D' band). **Figure 19(b)** shows the Raman spectrum of 1%CeO<sub>2</sub>/1%rGO/ZnO with characteristic peaks of graphene oxide peaks at 1350.87 cm<sup>-1</sup> (D band), 1605.74 cm<sup>-1</sup> (G band), 2684.22 cm<sup>-1</sup> (2D band) and characteristic peaks of ZnO and active modes F<sub>2g</sub>, CeO<sub>2</sub> (462.79 cm<sup>-1</sup>), where the I<sub>D</sub>/I<sub>G</sub> can be used to evaluate quantitative the crystallinity/disorder degree and are varying between 1.05 and 1.24, lower value indicates the less defects in graphitic structure [69]. **Figure 20** shows the morphologies for the three sensitive materials reveals for (a) CeO<sub>2</sub> was evidenced a polycrystalline structure, for (b) CeO<sub>2</sub>/rGO - the micrographic image presents a 3-D layered structured of GO mixed with small polycrystalline particles of ceria and for (c) CeO<sub>2</sub>/rGO/ZnO was evidenced a mixed polycrystalline structure of preponderant small particles of wurtzite hexagonal types ZnO and minor faces of cubic CeO<sub>2</sub> and carbon faces.



**Figure 19.** Raman spectra for rGO (a) and synthesized 1%CeO<sub>2</sub>/1%rGO/ZnO (b).

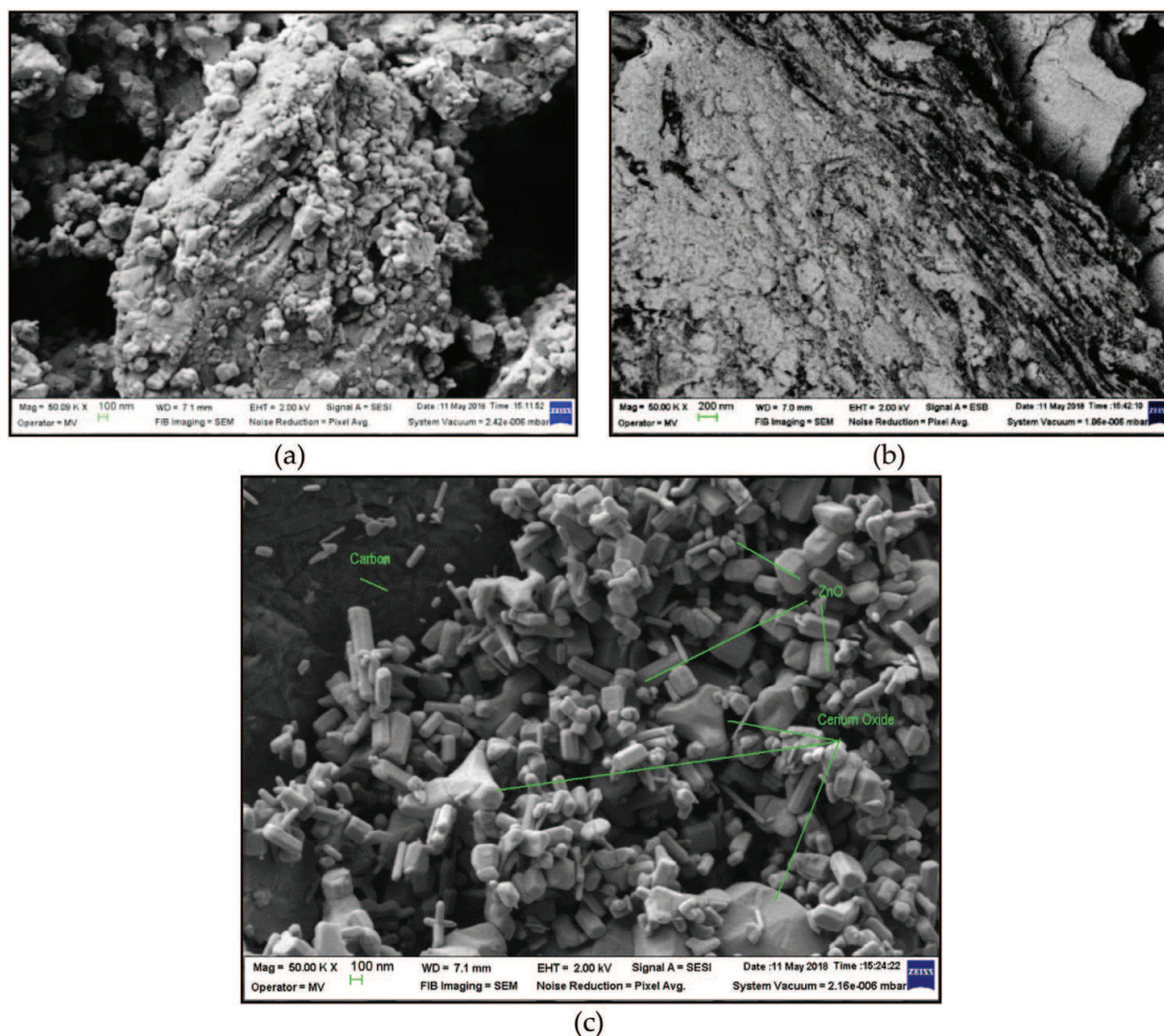


Figure 20. SEM images for: (a)  $\text{CeO}_2$ ; (b)  $\text{CeO}_2/\text{rGO}$ ; (c)  $\text{CeO}_2/\text{rGO}/\text{ZnO}$ .

#### 4.3. The construction of the sensing element for $\text{NO}_2$ gas detection designed with rGO-doped $\text{CeO}_2$ and $\text{CeO}_2$ -doped $\text{rGO}/\text{ZnO}$ sensitive material

The sensor module is constituted from printed circuit board (PCB), substrate with interdigitated Ag array electrode deposited by photolithographic technology and the sensitive material in amounts 15–20 mg was deposited on surface electrode. The active area for sensitive material was  $10 \text{ mm} \times 0.5 \text{ mm}$ , **Figure 21(a)** and **(b)**.

#### 4.4. The $\text{NO}_2$ gas sensing mechanism

In metal oxide semiconductor gas sensors, the resistance is measured as a function of the gas concentration. Generally, this devices function at elevated temperature between 200 and  $600^\circ\text{C}$  in air. The grain of metal oxide is covered by adsorbed oxygen molecules. Oxygen molecules present the character of electronegativity, they extract electrons from the conduction band of



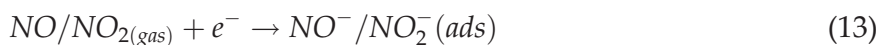


**Figure 21.** The NO<sub>2</sub> gas sensing element structure (a) PCB substrate with interdigitated Ag array electrode; (b) the sensing element made with PCB substrate and sensitive material deposited on surface electrode.

metal oxide causing the formation of oxygen ions  $O_2^-$ ,  $O^-$ ,  $O^{2-}$ , adsorbed at the surface of metal oxide. Since electrons are removed from the metal oxide, the concentration of free charge carriers is reduced forming a depletion layer at grain boundaries. The surface reactions can be written according with Eqs. (10–12):



As is it known, nitrogen oxides specify as NO<sub>x</sub> have the character of oxidizing gases with very high electron affinity 2.28 eV as compared with oxygen 0.43 eV. The NO<sub>x</sub> molecules interact with the surface of metal oxide through surface adsorbed oxygen ions, thus increasing the potential barrier at grain boundaries. The redox reactions taking place on the surface of a metal oxide can be written according with Eqs. (13–14) [70].



As result, the thickness and resistance of the depletion layer increase and resistance change is reversible at operating temperature [70]. The oxygen vacancies can significantly enhance the adsorption of oxygen molecules and electrons will transfer from the oxygen vacancies from CeO<sub>2</sub> to the oxygen molecules, resulting in more oxygen species (especially O<sup>2-</sup>). These oxygen species will react with NO<sub>2</sub>, resulting in an abrupt change in the conductivity of the sensor [71]. The graphene sheets by their good properties as: high surface area 2630 m<sup>2</sup>/g, thermal conductivity in the range of 3000–5000 W/mK at room temperature carrier mobility up to 200,000 cm<sup>2</sup>/Vs [72], electrical conductivity of 7200 S/m [73], coming from their structure two-dimensional (2D) single atom layer is used in gas sensing and in the composite leads to increase of the electrical conductivity of CeO<sub>2</sub> and thus improve the performance to gas sensing room temperature [71].

#### 4.5. The NO<sub>2</sub> gas sensors testing and sensing characteristics

The sensors with sensitive materials 1%rGO-doped CeO<sub>2</sub>, and 1% CeO<sub>2</sub>/1%rGO-doped ZnO were tested in NO<sub>2</sub> atmosphere in concentrations 5 and 10 ppm. The gas testing was effected

with testing installation presented in **Figure 4**. The gas testing was performed in order to establishment of the sensitivity sensors and response time. The sensor sensitivity was expressed in accord with Eq. (15), as the ratio of resistance in air to that in target gas, in this case NO<sub>2</sub>,

$$S = \frac{Ra}{Rg}$$
(15)

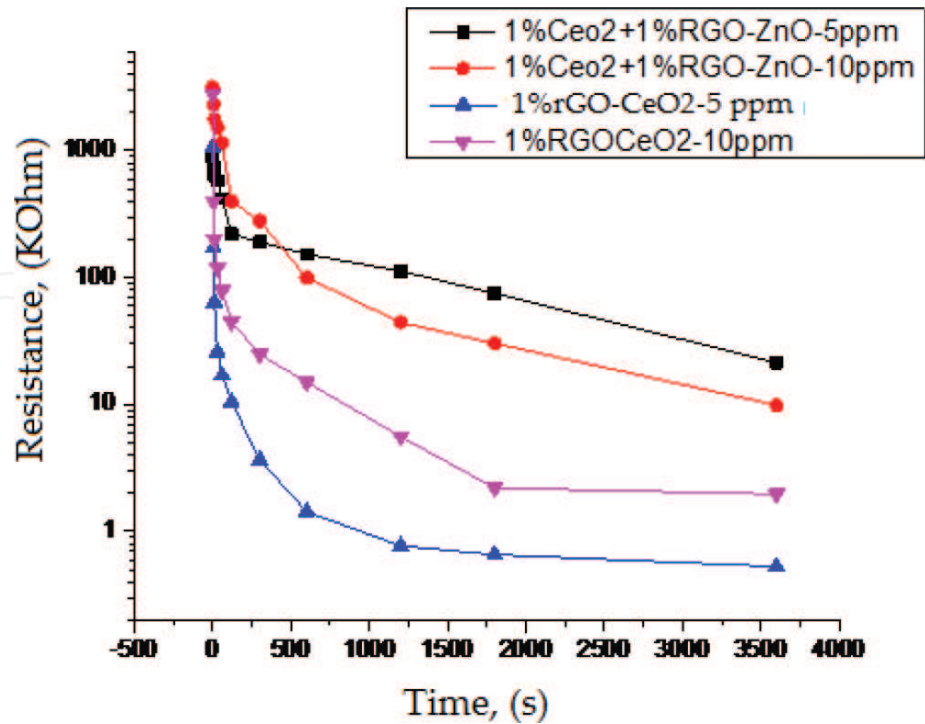
where *Ra* is the resistance of sensor in air and *Rg* is the resistance of sensor in gas.

The response time is expressed by formula:

$$Ra - 90\%x(Ra - Rg)$$
(16)

Notations are the same with Eq. (15) [28]. Having the resistance values, from the graph, the response time can be determined. **Figure 22** shows the resistance variation with time exposure gas and **Figure 23** shows the sensitivity (response) for sensing element with time exposure gas for two sensitive material: 1%rGO/CeO<sub>2</sub> and 1%CeO<sub>2</sub>/1%rGO/ZnO. All the characteristics are considered for the 1 hour time exposure. Since the resistance of sensors decreases sharply, for a good view we opted for a semilogarithmic scale representation of resistance and sensors response with exposure time. The decreases of resistance denotes a character of type p semi-conductors for both sensitive materials in oxidant gas like NO<sub>2</sub>, character given by reduced graphene oxide which is a semiconductor type p.

The sensors performances can be resumed in **Table 5**.



**Figure 22.** Resistance variation function with time.



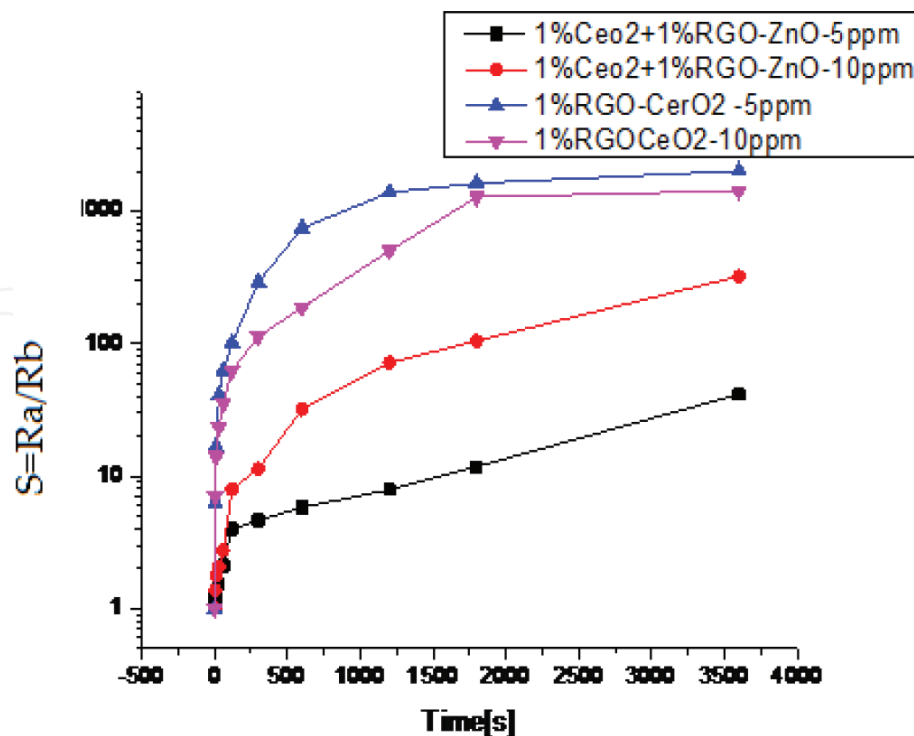


Figure 23. The sensitivity variation function with time.

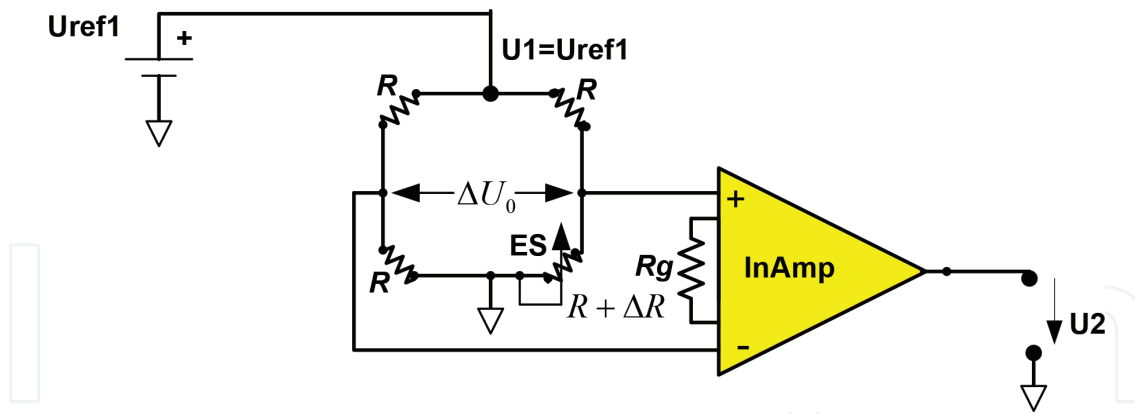
Sensitive material	Concentration NO <sub>2</sub> , [ppm]	Resistance in air, [kΩ]	Resistance in gas, [kΩ] (after 3600 s exposure)	Sensitivity, $R_a/R_g$	Response time, [s]
1%rGO/CeO <sub>2</sub>	5	1060	0.53	2000	2.5
1%CeO <sub>2</sub> /1%rGO/ZnO	5	885	21.43	41.29	2.8
1%rGO/CeO <sub>2</sub>	10	2800	1.54	1818	3.5
1%CeO <sub>2</sub> /1%rGO/ZnO	10	3180	9.9	321.2	2.2

Table 5. The characteristics of sensors with sensitive materials 1%rGO/CeO<sub>2</sub> and 1%CeO<sub>2</sub>/1%rGO/ZnO.

Analyzing the obtained results, it can be concluded that the both sensitive materials show the good performance at NO<sub>2</sub> exposure at room temperature. However, the sensitive material composed by 1%rGO/CeO<sub>2</sub> presents very good sensitivity at NO<sub>2</sub> exposure for 5 and 10 ppm concentrations of 2000 and 1818 and very short response time of 2.5 and 3.5 s. Thus, sensitive materials with CeO<sub>2</sub> in majority concentration in matrix with reduced oxide graphene presents the best performance at NO<sub>2</sub> detection, face to sensitive materials 1%CeO<sub>2</sub>/1%rGO/ZnO where ZnO is majority and are a promising sensitive materials for NO<sub>2</sub> detection.

#### 4.6. Signal conditioning of the sensing element for NO<sub>2</sub> gas detection designed with rGO-doped CeO<sub>2</sub> and CeO<sub>2</sub>-doped rGO/ZnO sensitive material

Resistance of sensor sensing element ES,  $R + \Delta R$ , Figure 24 may vary from less than 10 kΩ to several hundred kΩ, depending on the design of the sensor and the physical environment to



**Figure 24.** Schematic of the electronic block for signal conditioning generated by the sensing element.

be measured. The sensing element ES of the NO<sub>2</sub> gas sensor is disposed in one of the Wheatstone bridge arms and shows the resistance R for a NO<sub>2</sub> concentration of zero ppm. The resistances of resistors disposed in all of other branches of the bridge show the same value, namely R. A DC voltage excitation source U1 is connected to one of the bridge diagonals [74].

If the gas concentration of NO<sub>2</sub> is zero ppm, the sensing element ES shows the resistance R. The Wheatstone bridge is in this case at equilibrium so that the voltage measured on the other diagonal of the bridge is 0 V. Variation of NO<sub>2</sub> gas concentration in the range from zero ppm to 10 ppm causes a voltage variation with  $\Delta U_0$ , which can be measured on the other diagonal of the bridge. The voltage variation up to  $\Delta U_0$  is given by the relation (17):

$$\Delta U_0 = \frac{U1}{2} \left[ \frac{\frac{\Delta R}{2}}{R + \frac{\Delta R}{2}} \right] \quad (17)$$

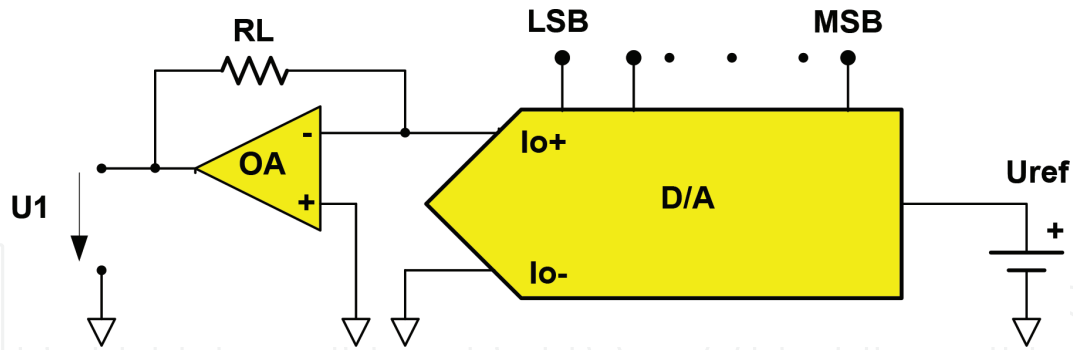
The operational amplifier that can be used with the best performance is instrumentation type amplifier (in-amp), “resistor programmable” (**Figure 24**). Considering the transfer function of the electronic amplifier module and taking into account the relation (17), we obtain [74]:

$$U2 = \frac{U1}{2} \left[ \frac{\frac{\Delta R}{2}}{R + \frac{\Delta R}{2}} \right] A = K \left[ \frac{\frac{\Delta R}{2}}{R + \frac{\Delta R}{2}} \right], \quad (18)$$

where A is the amplification factor, depending on the  $R_g$  resistance value and  $K = \frac{U1}{2} A$ , is a constant. In-amps such as the AD620 family, the AD623 and AD627, Analog Devices type can be used in single (or dual) supply bridge applications.

#### 4.6.1. Realization of the continuous U1 excitation voltage source

The continuous U1 excitation voltage source is made using a D/A digital/analog converter, a Uref reference voltage and an operational amplifier (OA) (**Figure 25**). Thus, depending on the values set for the least significant bit (LSB) up to the most significant bit (MSB), the resulting word can establish a desired U1 continuous excitation voltage. **Figure 25** shows the schematic of the electronic block for the U1 excitation voltage source.

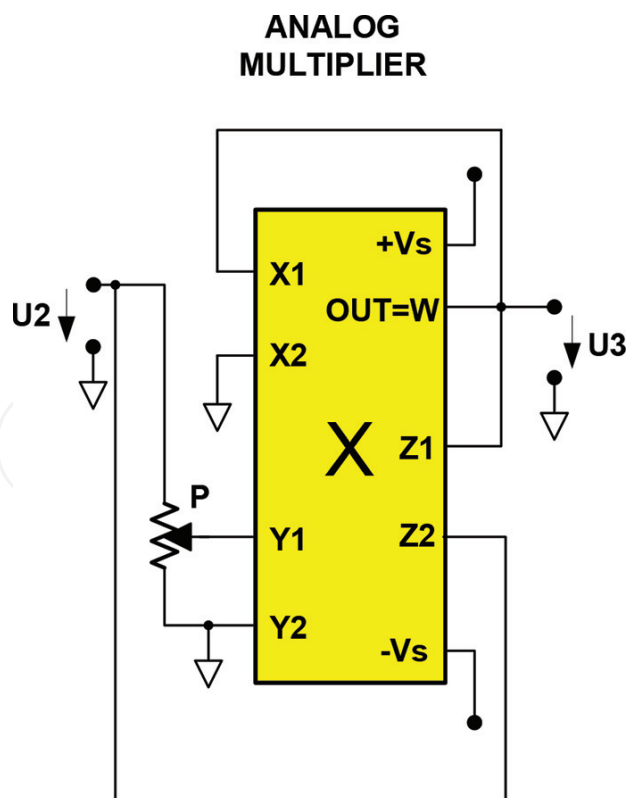


**Figure 25.** Schematic of the electronic block for the U1 excitation voltage source.

#### 4.6.2. Bridge-linearization electronic circuit

Schematic of the electronic linearization block of the signal generated by the Wheatstone bridge, via an operational amplifier, in-amp uses an analog multiplier [75], AD 534 or AD 734, produced by analog devices (**Figure 26**). The transfer function associated with the AD 534 or AD 734 analog multiplier is written [76, 77]:

$$W = A_0 \left\{ \frac{(X1 - X2)(Y1 - Y2)}{SF} - (Z1 - Z2) \right\} \quad (19)$$



**Figure 26.** Schematic of the electronic linearization block of the signal generated by the Wheatstone bridge, via an operational in-amp instrumentation amplifier.

where  $A_0$  is the open loop gain,  $X1$ ,  $X2$ ,  $Y1$ ,  $Y2$ ,  $Z1$  and  $Z2$  represent the inputs of the analog multiplier,  $SF$  a scale factor, typically  $SF = 10$  V and  $W = OUT$ , according to **Figure 26**.

Since  $A_0 \rightarrow 72$  dB can be considered as  $W/A_0 \rightarrow 0$  and the relation (19) becomes:

$$(X1 - X2)(Y1 - Y2) = SF(Z1 - Z2) \quad (20)$$

Since  $Z1 = W$  it is obtained:

$$W = \frac{(X1 - X2)(Y1 - Y2)}{SF} + Z2 \quad (21)$$

Since  $Z2 = U2$ ,  $Y1 - Y2 = \beta U2$ ,  $0 \leq \beta < 1$ ,  $X2 = 0$  and  $X1 = Z1 = W = U3$ , according to **Figure 26**. Finally,

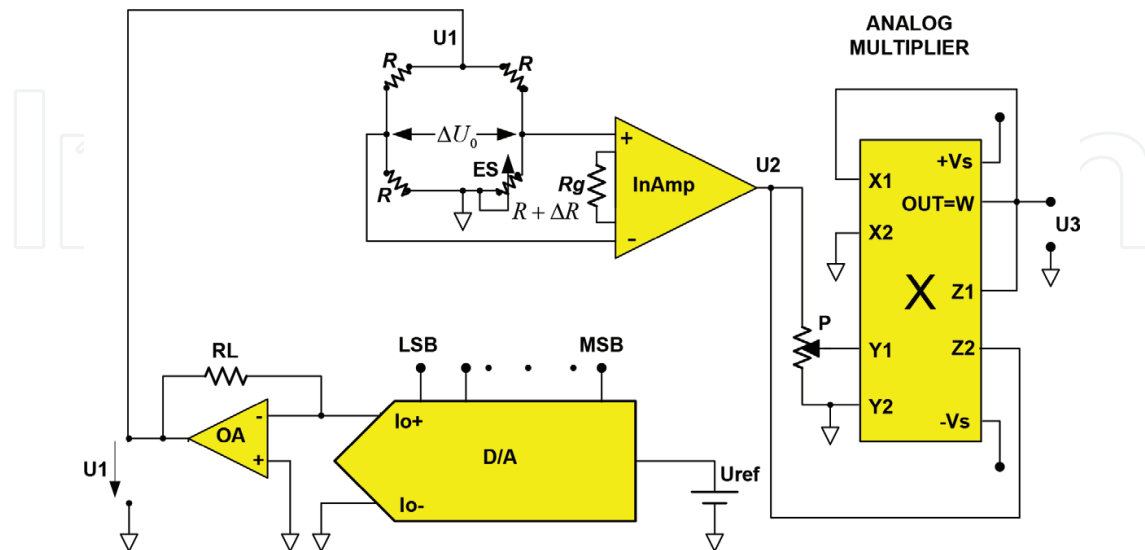
$$U3 = W = \frac{U2}{1 - \frac{\beta U2}{SF}} \quad (22)$$

is obtained

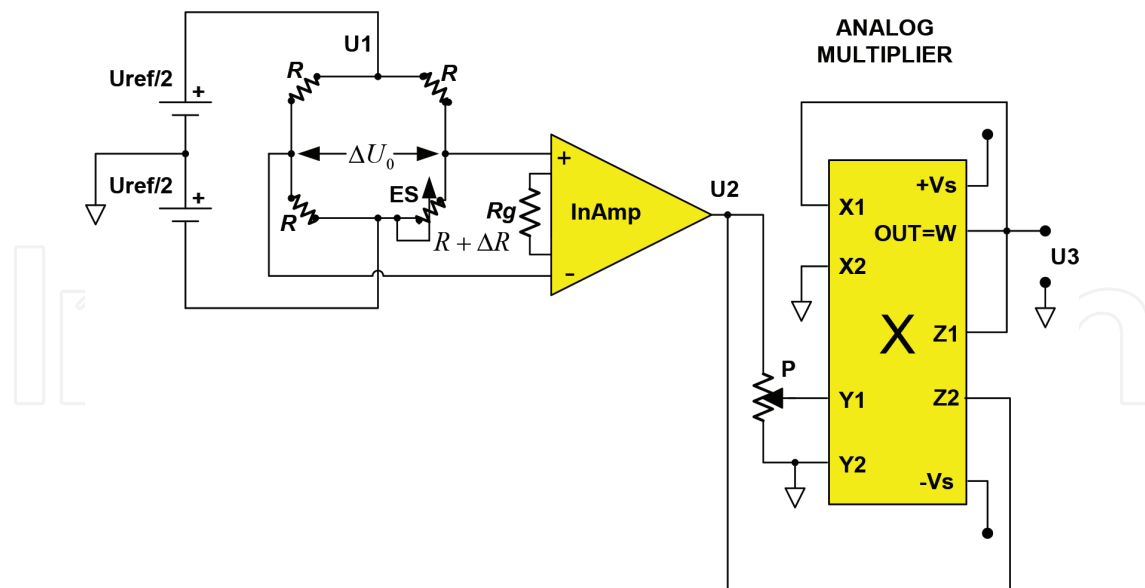
The relation (6) together with the relation (2) represents the calculation method regarding the linearization of the signal generated by the Wheatstone bridge, via an operational in-amp instrumentation amplifier.

#### 4.6.3. Resulting structures for the electronic block for signal conditioning generated by the sensing element

By considering the three previously analyzed electronic blocks, the electronic block for signal conditioning generated by the sensing element is obtained. **Figure 27** shows the schematic of



**Figure 27.** Schematic of the electronic block for signal conditioning generated by the sensing element, single supply bridge applications.



**Figure 28.** Schematic of the electronic block for signal conditioning generated by the sensing element, dual supply bridge applications.

the electronic block for signal conditioning generated by the sensing element, single supply bridge applications.

It is possible to reconfigure circuits so as to improve the performance in terms of reduces the dc common-mode voltage to zero. **Figure 28** shows how the use of split U1 tension in order to reduce the dc common-mode voltage to zero.

An isolation amplifier can be useful for this application, with respect to the signal-conditioning, so that it does not exist galvanic connections between the bridge and grounded instrumentation circuitry.

## 5. Conclusions

Cerium, by its unique electronic configuration ([Xe] 4f<sup>2</sup>6s<sup>2</sup>) and by the two common valence states Ce<sup>3+</sup> and Ce<sup>4+</sup> allowing a redox reaction between them which gives CeO<sub>2</sub> excellent chemical and physical properties, is used in many applications, like as: three-way catalytic reactions to eliminate toxic automobile exhaust, the low-temperature water gas shift reaction, oxygen permeation membrane systems for fuel cells as well as gas sensors. For gas sensing applications, several sensitive elements based on CeO<sub>2</sub> were tested to determine both this detection function as well as this performances:

- By doping the CeO<sub>2</sub> with oxides semiconductor, for example, Nb<sub>2</sub>O<sub>5</sub> introduced in CeO<sub>2</sub> structure, the following mechanism is triggered: Nb<sup>5+</sup> ions initiate the reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> resulting in the formation of oxygen vacancies with consequences in increasing the sensitivity.
- The ionic conductivity of CeO<sub>2</sub> is improved by doping with rare earth oxides such as Sm<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub>. The size of conductivity for doped ceria depends on the ionic



radius of the doping ion. Therefore, the introduction of trivalent ions in ceria leads to the production of anion vacancies which may enhance catalytic and gas sensing.

- CO<sub>2</sub> detection using sensitive material based on mixed binary oxide CeO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub> in ratio 97%/3%, for 10,000 ppm CO<sub>2</sub> at the 25, 50 and 70°C chamber test temperature, the sensor was developed voltage values of 48, 50 and 770 mV.
- CO<sub>2</sub> detection with Y<sub>2</sub>O<sub>3</sub>-doped CeO<sub>2</sub> molar ratio CeO<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub> = 4:1 with characteristics: the CO<sub>2</sub> concentration in the range of 0–5000 ppm, function temperature 135°C, climatic conditions  $T = 20^{\circ}\text{C}$ , 40% RH and 80% RH, voltage values 378.17–377.32 mV for  $T = 20^{\circ}\text{C}$ , 40% RH and 377.11–376.61 for  $T = 20^{\circ}\text{C}$ , 80% RH. Sensitivity is 0.3 V/ppm and response time 30 seconds;
- Sensitive materials based on 1%rGO/CeO<sub>2</sub> and 1%CeO<sub>2</sub>/1%rGO/ZnO was analyzed with UV-Vis spectroscopy showing that a decreasing of band gap of CeO<sub>2</sub> in matrix with rGO from 3.19 eV at 3.05 eV what allows for sensor to function at room temperature. The sensors were tested for 5 and 10 ppm NO<sub>2</sub> obtaining the sensitivities of 2000 and 1818, response times of 2.5 and 3.5 s for sensitive material 1%rGO/CeO<sub>2</sub> and sensitivities of 41.29 and 321.2, response times of 2.8 and 2.2 s for sensitive material 1%CeO<sub>2</sub>/rGO/ZnO. The sensitive materials made so that the matrix in which CeO<sub>2</sub> is in majority presents the best performance.
- Also, the sensing mechanism in CO<sub>2</sub> and NO<sub>2</sub> detection was discussed.

Based on these results, it can be stated that CeO<sub>2</sub> is a good candidate in gas sensors applications.

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## Conflict of interest

No conflict of interest exists with regard to this chapter.

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