

Research Article

Synthesis and Structural Investigations of Ag-Added BaTiO₃-CuO Mixed Oxide for CO₂ Gas Sensing

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Compositions having the general formula BaTiO₃-CuO + x wt% Ag, where $x = 0, 1, 1.5,$ and 2 have been prepared by solid state ceramic processing and sintered at 500 and 700°C for 5 h. Thermogravimetric analysis (TGA), X-ray powder diffraction (XRD), infrared absorption spectra (IR), and scanning electron microscopy (SEM) were used to characterize the obtained sensor pellets. It was found that no solid state reaction took place between BaTiO₃ and CuO during sintering process. The sensitivity of the prepared sensors to CO₂ gas increases with increasing sintering temperature and Ag content. The correlation between Ag content at different sintering temperature and structure characterization is discussed.

1. Introduction

Atmospheric pollution is defined as a status containing gases, offensive odors, and particles that are harmful to human, animals, vegetables, or living environments above the regulation limits in specific regions [1]. A severe phenomenon of the environment is global warming. This phenomenon is considered to be related to the aspect that the concentration of carbon dioxide in the atmosphere is increasing. The ideal chemical gas sensor must be chemically selective, reversible, fast response, highly sensitive, no contaminating, no poisoning, simple using, small size, simple fabrication, relative temperature insensitivity, low noise and low manufacturing costs [2]. While in all the mentioned cases it would be valuable to have a low-cost sensor. Nonexpensive and robust detection systems are required for air quality, food control, and early fire detection. Gas sensors monitoring CO₂ concentrations are used in fields such as agricultural industries, biotechnological processes, air conditioning, medical services, housing, and environmental observation [3]. Most of the currently available sensing systems are based on optical detection, which makes them expensive. Some cheaper electrochemical sensors have also been developed, but their fabrication process is still complicated. Moreover, in the presence of humidity, these sensors reduce drastically

their response to CO₂. In this situation, solid-state gas sensors based on semiconductor metal oxides may be a promising alternative, since they offer good sensor properties and can be easily mass-produced. Semiconductor gas sensors based on the capacitance or resistance change of the sensor are good candidates to reach a reliable and cheap sensor for CO₂. The gases' adsorption or their reaction on the surfaces of the semiconducting materials induces the change in the density of the conducting electrons in the polycrystalline sensor elements. Several oxides have been tested, and La-doped SnO₂ and BaTiO₃ are reported to be the most reliable options for CO₂ detection [4–6]. However, comparison of the responses of SnO₂-doped sensors reveals discrepancies in the resistance variation.

The present work aims to synthesize BaTiO₃-CuO mixed oxide sensors sintered at different temperature and to study the effect of sintering temperature and Ag content on the sensors structure and the sensitivity to CO₂ gas.

2. Experimental

2.1. Samples Preparation. The BaTiO₃ powder used in this investigation was prepared by the solid state reaction method using BaCO₃ (99.7% purity) and TiO₂ (99.8% purity) in the

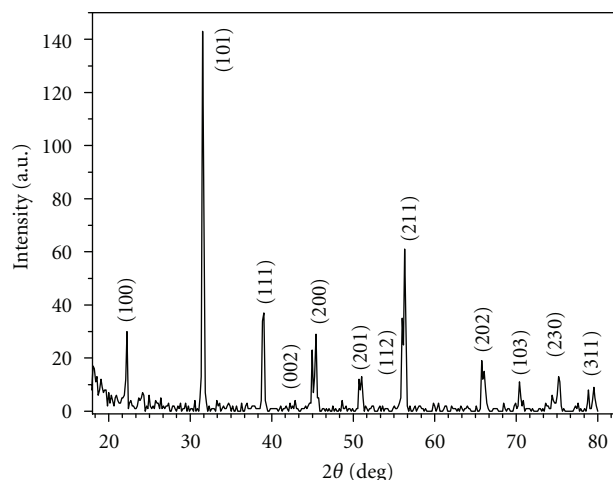


FIGURE 1: X-ray diffraction pattern of the prepared BaTiO₃.

molar ratio of 1:1. The mixed powder was calcined in a platinum crucible at 800°C for 2 h and then heated for 8 h at 1200°C in air atmosphere. Finally, the powder was then left to cool inside the furnace in the same atmosphere. The produced BaTiO₃ powder was investigated by XRD which confirmed the formation of BaTiO₃ as a tetragonal single phase (Figure 1). The BaTiO₃-CuO-based sensor samples were prepared by mixing the obtained BaTiO₃ and CuO powders (99.8% purity) in 1:1 molar ratio. The mixture was mechanically mixed thoroughly in an agate mortar for 24 h. Samples of BaTiO₃-CuO with silver additions were prepared by adding silver nitrate (AgNO₃) to the mixture of BaTiO₃ and CuO in different ratios to obtain Ag content after sintering processes with the concentration of 1, 1.5, and 2 wt%. The resulting powders were mixed thoroughly in presence of distilled water to improve homogeneity. The materials were pressed to form pellets of 16 mm in diameter and 1 mm thickness by applying a pressure of 7.5 ton/cm². The prepared samples were dried overnight at 70°C. The drying temperature was raised at a rate of 5°C/h to reach 100°C then left overnight, to avoid crack formation. The samples were divided into two groups; the first group was sintered at 500°C for 5 h in an electric furnace, while the second group was sintered at 700°C for 5 h, each in air atmosphere. Finally, the samples were then left to cool inside the furnace.

2.2. Characterization. All the prepared samples were investigated by X-ray powder diffraction analysis (XRD) using X-ray diffractograms provided with a computer-controlled X-ray diffractometer (model-Bruker AXS D₈ advance), and copper radiation Cu K α with nickel filter was used. Thermogravimetric analysis (TGA) for the silver nitrate, starting materials, and BaTiO₃-CuO mixture was carried out using an automatic recording thermobalance type (Shimadzu DTA-50). The rate of heating was 10°C/min in the range from 30 up to 800°C. The infrared absorption spectra (IR) measurements in the range of 2000–200 cm⁻¹ were performed by KBr method using Nexus 670 FT-IR spectrophotometer (Nicolet, USA). Scanning electron

micrographs of the prepared samples were obtained using scanning electron microscopy (SEM JEOL models, JXA-480A Electron Probe Micro analyzer). Electrical conductivity as well as capacitance changes and sensing characteristics to CO₂ gas for different prepared samples were also carried out. The sensitivity to CO₂ gas was defined as the ratio of the capacitance of the sensor sample on exposure to air with known concentration of gas to that in air stream namely: $\text{sensitivity} = C_{\text{CO}_2}/C_{\text{air}}$, and the details of these measurements are given elsewhere [7].

3. Results and Discussion

3.1. X-Ray Diffraction Analysis (XRD). X-ray diffraction analysis of the prepared BaTiO₃ and CuO used revealed that BaTiO₃ has only single phase with tetragonal structure (Figure 1). While CuO, Figure 2, has a monoclinic structure ($a = 4.653 \text{ \AA}$, $b = 3.41 \text{ \AA}$, and $c = 5.108 \text{ \AA}$) according to ICSD cards, no characteristic peaks of any impurities were observed. The X-ray diffraction patterns of the BaTiO₃-CuO-based sensor samples as well as Ag-doped samples sintered at 700°C are shown in Figure 3. With respect to the undoped sample, no diffraction peaks except for those from BaTiO₃ and CuO were observed and no changes in the diffraction angles nor in the relative intensities of each diffraction peaks due to BaTiO₃ and CuO can be recognized [8, 9]. This means that no solid reaction took place between BaTiO₃ and CuO during the sintering process at 500 and 700°C and the prepared BaTiO₃-CuO sample is only a mixture having two phases. The patterns of the samples with silver additions of 1.5 and 2 wt% revealed a weak peak at $2\theta = 38.6$ ($d = 2.35 \text{ \AA}$) which coincide with the 100% peak of silver ($d = 2.359 \text{ \AA}$, ICSD card) [10]. X-ray instrument with computer program was used to calculate the crystallite sizes of each component (BaTiO₃, CuO, and Ag) in the samples sintered at different temperatures. It was found that the crystallite size of the BaTiO₃ lies in the range from 132 to 140 nm and from 158 to 168 nm for the samples sintered at 500 and 700°C, respectively, while the crystallite size of the CuO lies in the range from 70.1 to 74.8 nm and from 90.3 to 95 nm for the samples sintered at 500 and 700°C, respectively. The crystallite size of Ag-added was estimated from the 100% peak of silver which appeared in X-ray diffraction patterns of the samples with 1.5 and 2 wt% Ag additions, and the obtained values are presented in Table 1. It was found that the average crystallite size of silver particles is 241.9 nm in the sensor samples sintered at 500°C, while the samples sintered at 700°C gave an average value of 335.5 nm. This indicates that the crystallite sizes slightly increased with increasing the sintering temperature for all components in the prepared sensor samples as shown in Table 1.

3.2. Thermogravimetric Analysis (TGA). The thermogravimetric (TG) curves of (a) silver nitrate, starting material, and (b) BaTiO₃-CuO mixture in the temperature range from 30 up to 800°C are shown in Figure 4. The TG curve of silver nitrate shows a large weight loss between 400 and 500°C then after no further weight loss up to 800°C. Silver nitrate is

TABLE 1: Average crystallite sizes of the sensor samples components sintered at different temperatures.

Samples	Sintering temperature (°C)	Crystalline size (nm)		
		BaTiO ₃	CuO	Ag
BaTiO ₃ -CuO	500	132	70.1	—
BaTiO ₃ -CuO + 1 wt%Ag	500	138	74	—
BaTiO ₃ -CuO + 1.5 wt%Ag	500	134	70.1	237
BaTiO ₃ -CuO + 2 wt%Ag	500	140	74.8	245
BaTiO ₃ -CuO	700	158	90.3	—
BaTiO ₃ -CuO + 1 wt%Ag	700	161	91.2	—
BaTiO ₃ -CuO + 1.5 wt%Ag	700	165	92.7	335.4
BaTiO ₃ -CuO + 2 wt%Ag	700	168	95	335.6

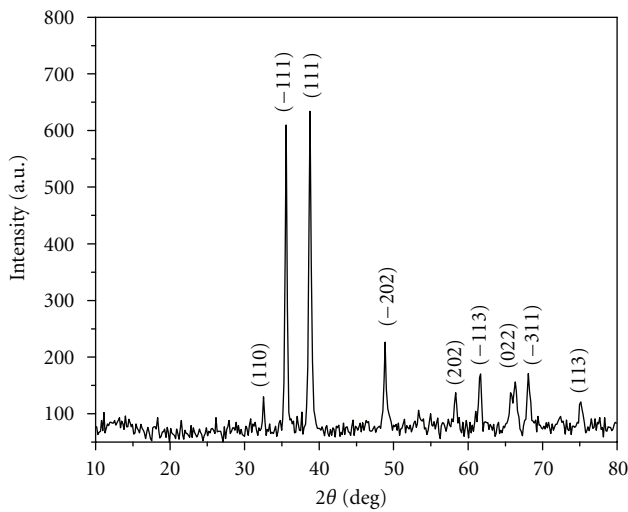


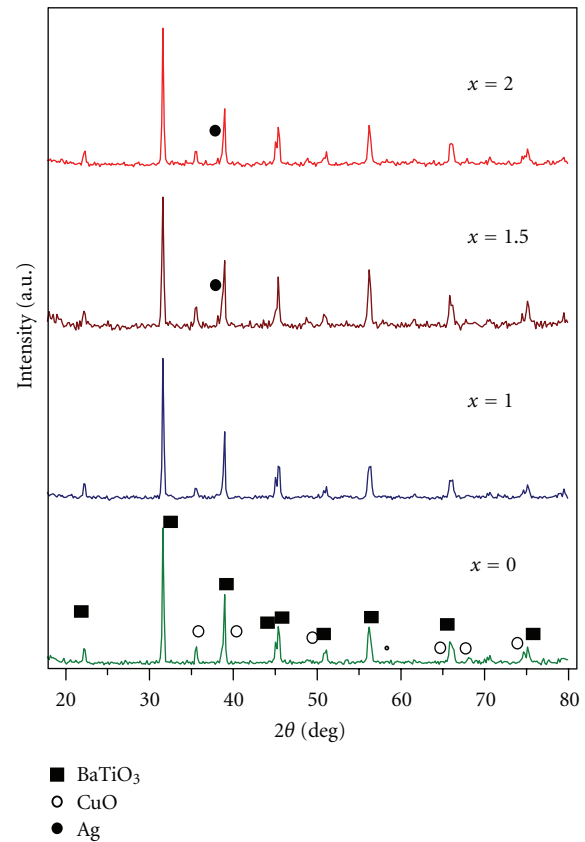
FIGURE 2: X-ray diffraction pattern of CuO.

the most stable nitrate known, and it can be melted without decomposition. L'vov et al. [11] reported that silver nitrate melts at 210°C and subsequently decomposes at 440°C to yield silver according to the following equation:



Thus, the observed weight loss (Figure 4(a)) is due to the decomposition of silver nitrate which produced silver particles. There is no observed weight loss in BaTiO₃-CuO mixture curve (Figure 4(b)) which indicates that this mixture is thermally stable in the temperature range from 30 up to 800°C and there is no any chemical reaction between the two components took place. According to these results, the silver nitrate added to BaTiO₃-CuO mixed oxide and after sintering at 500 and 700°C transformed into silver particles which was also confirmed by the X-ray diffraction investigation.

3.3. Infrared Absorption Spectra (IR). The IR absorption spectra at room temperature of (a) the prepared BaTiO₃ and (b) CuO used are shown in Figure 5. The bands position and their intensities were automatically recorded, and it was indicative that no further detectable bands above 2000 cm⁻¹

FIGURE 3: X-ray diffraction patterns of BaTiO₃-CuO + x wt% Ag samples sintered at 700°C.

were observed. The spectrum of BaTiO₃ (Figure 5(a)) shows two main absorption bands below 1000 cm⁻¹. The bands appearing at 550 cm⁻¹ and around 400 cm⁻¹ are assigned as ν_1 and ν_2 , respectively. The X-ray investigation carried out on this sample confirmed that it has tetragonal structure. Thus, the higher frequency band (ν_1) can be attributed to the Ti-O stretching vibration and the other band (ν_2) to Ti-O bending vibration. The obtained data are in agreement with that reported by different authors [12, 13] for BaTiO₃ prepared in air atmosphere. With respect to CuO (Figure 5(b)), the IR spectrum at room temperature showed four absorption bands below 1000 cm⁻¹. These bands are observed at 580, 500, 420, and 320 cm⁻¹, respectively, which can be attributed

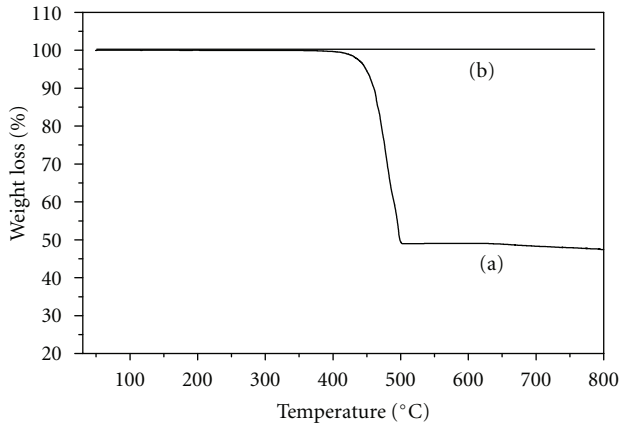


FIGURE 4: TG curves of (a) silver nitrate and (b) BaTiO₃-CuO mixed oxides.

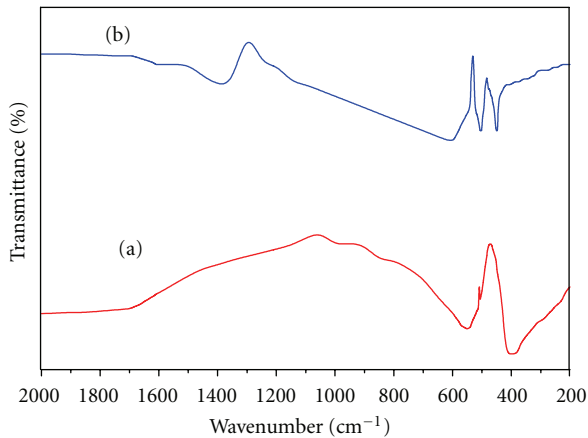
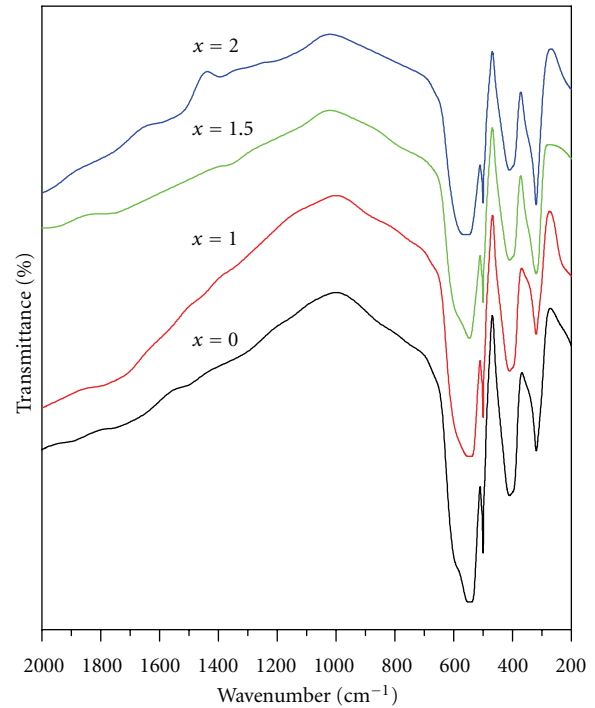
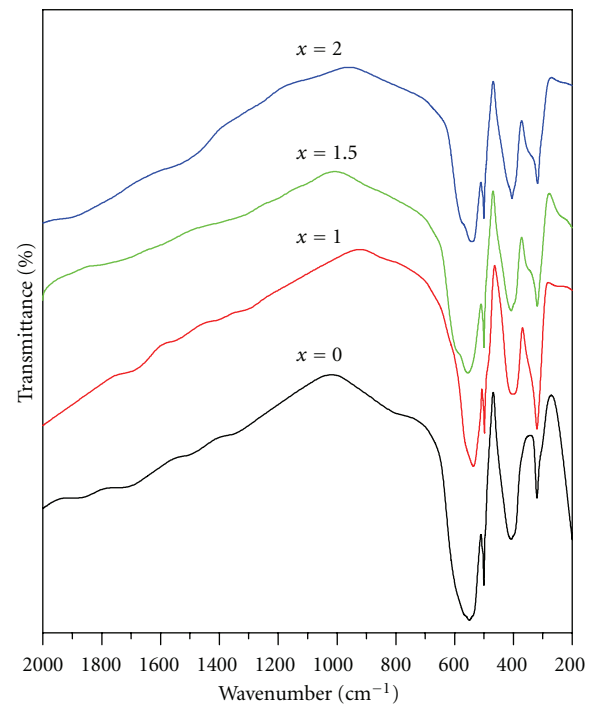


FIGURE 5: IR absorption spectra of (a) BaTiO₃ and (b) CuO.

to Cu-O stretching modes. This result is in accordance with that obtained by the different authors [14, 15]. The infrared absorption spectra of BaTiO₃-CuO mixed oxide samples as well as Ag-added samples sintered at 500 and 700°C are shown in Figure 6. The IR spectra of BaTiO₃-CuO samples sintered at different temperature look like a combination of the spectra of BaTiO₃ and CuO. This was expected since no chemical reaction took place between the two components as explained from X-ray investigation. The vibrational band of CuO that appeared at 580 cm⁻¹ (Figure 5(b)) cannot be observed in the IR spectra of mixed oxide samples (Figure 6). This may be due to the presence of a broad band which is attributed to Ti-O stretching vibration of BaTiO₃ which extended from about 510 to 620 cm⁻¹ with a centre at 550 cm⁻¹. The two bands that appeared around 500 and 320 cm⁻¹ are due to Cu-O stretching vibration of CuO [16]. The second broad band of BaTiO₃ appeared at 400 cm⁻¹ overlap with that at 420 cm⁻¹ of CuO to give one peak at about 410 cm⁻¹ in all mixed oxide samples. The IR spectra of the pure mixed oxide samples sintered at 500 and that at 700°C were found to exhibit the same number of the bands in the same position with slightly more sharpness as increasing the sintered temperature. The spectral data resulting from



(a)



(b)

FIGURE 6: IR absorption spectra of BaTiO₃-CuO + *x* wt% Ag samples sintered at (a) 500°C and (b) 700°C.

Ag addition with the concentrations of 1, 1.5, and 2 wt% can be shown in Figure 6. It can be seen that only a slight shift in bands position toward lower frequencies occurred with increasing Ag content. The observed shift may be due to the effect of Ag on metal-oxygen bonds vibration of both BaTiO₃ and CuO.

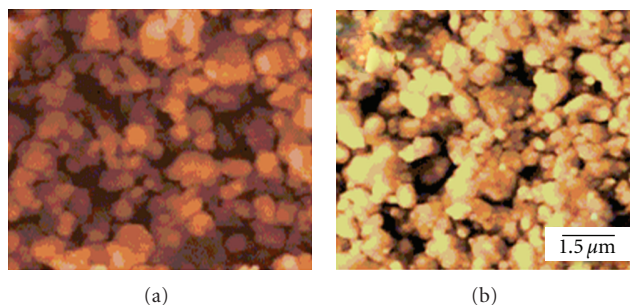


FIGURE 7: Scanning electron micrographs of the prepared (a) BaTiO₃ and (b) CuO.

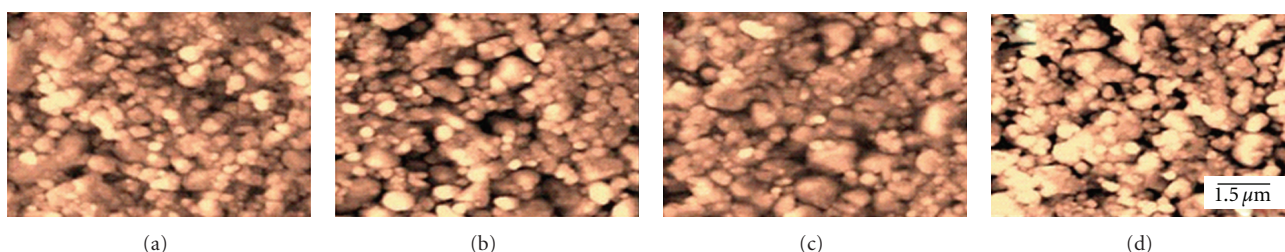


FIGURE 8: SEM micrographs of BaTiO₃-CuO + x wt% Ag sensors sintered at 700°C, (a) $x = 0$, (b) $x = 1$, (c) $x = 1.5$, and (d) $x = 2$.

3.4. Scanning Electron Microscopy (SEM). The scanning electron microscopy investigation carried out on the present samples explained that, with increase of sintering temperature from 500 to 700°C, the average grain size of the samples relatively increased. The scanning electron micrographs of the prepared BaTiO₃ and CuO samples used in this study are shown in Figure 7. The micrograph of BaTiO₃ sample (Figure 7(a)) shows a modestly uniform grained microstructure and nearly flat grain edges with some pores at grain boundaries. The micrograph of CuO (Figure 7(b)) shows irregular morphology with some pores at grain boundary and little fine pores entrapped within the grains. It can also be seen that BaTiO₃ sample has larger grain size than that of CuO. The SEM micrographs of pure and Ag-added BaTiO₃-CuO samples sintered at 700°C are shown in Figure 8. With respect to pure sample, Figure 8(a), the presence of BaTiO₃ grains and the smaller CuO grains is clearly observed with some pores at grain boundaries. Also, the clods of BaTiO₃ grains just contact mechanically to those of CuO. The obtained result is in agreement with that obtained by Ishihara et al. [17] for BaTiO₃-CuO mixed oxide. The particle morphology of Ag-added samples (Figures 8(b), 8(c), and 8(d)) varied with the composition where surface softness and particles sphericity improved with increasing Ag content. Also, the average particle size was found to increase with Ag content. Majumdar et al. [18] reported that the morphology of Ag-CuO particles was distinct that the silver in these particles was not encased in a metal oxide matrix, though the silver filled the voids of porous copper II oxide shell.

3.5. Sensitivity to CO₂ Gas. Electrical conductivity as well as capacitance changes and sensing characteristics to CO₂

gas measurements for the different prepared samples were also carried out. The capacitance measurements were used to characterize the sensitivity of the sensor samples. The results lead to conclude that the electrical conductivity of BaTiO₃-CuO sensors which have p-n junction units increases with sintering temperature and Ag content. The addition of Ag prolonged the response time of the sensors on exposure to CO₂ gas, while the recovery time during reexposure to air was 300 second. The details of these measurements and their results and discussion are given in a previous publication [7].

The variation of the sensitivity to CO₂ gas of the prepared sensors with Ag content at different sintering temperature is shown in Figure 9. A large increase in the sensitivity of the sensors with increasing the sintering temperature from 500 to 700°C was found. This may be due to the higher dispersion of Ag particles which are attained by sintering at higher temperature where the decomposition of AgNO₃, starting material is promoted by increasing the sintering temperature. Jiao et al. [19] stated that, low a sintering temperature or too short sintering time is disadvantageous to the decomposition and separation of AgNO₃. So the increase in the sensitivity with silver additions may be due to the role of silver as a catalytic one on the surface of BaTiO₃-CuO through the formation and decomposition of silver carbonates which leads to the significantly increasing sensitivity.

4. Conclusions

XRD and IR investigations confirmed that no solid reaction took place between BaTiO₃ and CuO during the sintering process (500–700°C), and the prepared BaTiO₃-CuO sample is only a mixture of two phases. The crystallite size was found to increase with sintering temperature for all components

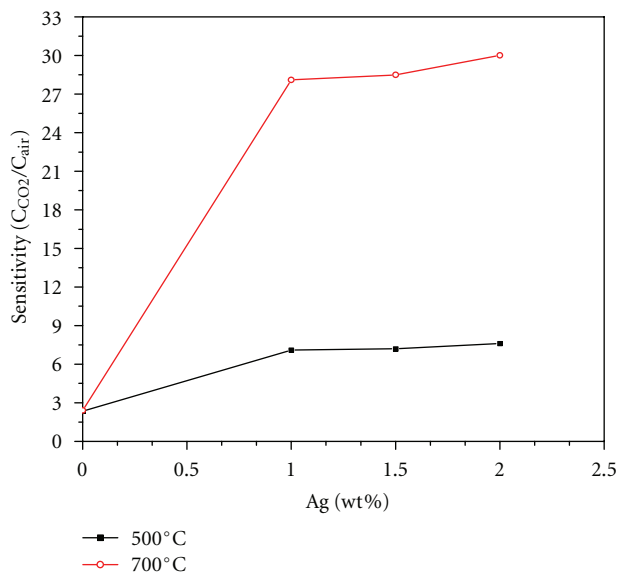
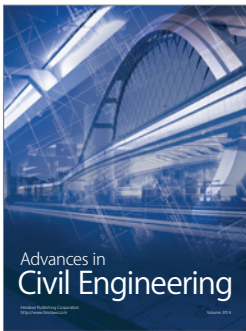
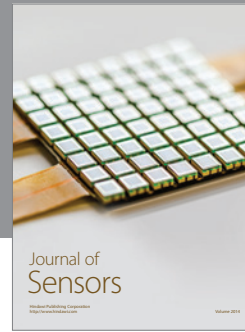
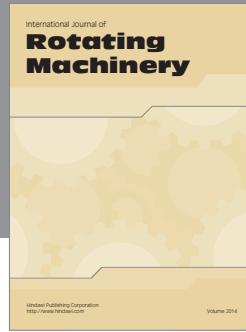


FIGURE 9: Variation of the sensitivity to CO₂ gas of BaTiO₃-CuO sensors with Ag content at different sintering temperatures.

in the samples. TG analysis revealed that these samples are thermally stable under high temperature measurements (up to 800°C). The particles morphology of the present samples is sensitive to silver content and sintering temperature. The sensitivity of the prepared samples to CO₂ gas increases with increasing sintering temperature and Ag content.

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