INFLUENȚA POROZITĂȚII ŞI A TEMPERATURII DE LUCRU ASUPRA SENSIBILITĂȚII LA UMIDITATE A SENZORILOR DE TITANAT DE BARIU CU ADAOS DE GRAFIT

THE EFFECT OF POROSITY AND WORKING TEMPERATURES ON THE HUMIDITY SENSITIVITY PROPERTIES OF BARIUM TITANATE SENSORS WITH GRAPHITE ADDITIVE

BURCU ERTUĞ*
Istanbul Technical University, Department of Metallurgical and Materials Eng., Istanbul, Turkey.

Porous barium titanate ceramics were produced by solid state synthesis. Stoichiometric amounts of high-purity powders containing 0.18 wt.% of La_2O_3 were mixed by ball-milling. The resultant mixtures were dried, sieved and were cold pressed into green samples then sintered at 1200-1500℃ for 6h. in air to form the perovskite phase. The porosity of the sintered bars were measured by Archimedes method. The obtained ceramics were characterized by SEM. The average grain size values and microstructural features were determined for four different compositions. The electrical conductivity values were measured under humid environment and transformed into humidity sensitivity values. Effects of porosity and working temperatures on porous barium titanate ceramics were investigated and results were evaluated in terms of microstructure.

Materiale ceramice poroase pe bază de titanat de bariu au fost preparate prin sinteza în fază solidă. Cantități stoichiometrice de pulberi precursoare de puritate ridicată, conținând 0,18 %m La_2O_3, au fost amestecate într-o moară cu bile. Amestecul rezultat a fost uscat, sitat şi presat la rece după care a fost sinterizat la 1200-1500^{0}C timp de 6h. Porozitatea corpurilor sinterizate a fost măsurată prin metoda Archimedes. Materialele ceramice au fost caracterizate prin SEM. Dimensiunea medie a granulelor precum şi caracteristicile microstructurale au fost determinate pentru patru compoziții diferite. Valorile conductivității electrice au fost determinate în condiții de umiditate şi transformate în valori de sensitivitate. S-au investigat efectele porozității şi temperaturii de procesare asupra materialelor ceramice poroase de titanat de bariu iar interpretarea rezultatelor a fost corelată cu microstructura.

Keywords: *Barium titanate, sintering, graphite, electrical conductivity, humidity sensitivity.*

1. Introduction

The automatic control technology provides human control over industries where physical abilities such as high speed, greater force and especially sensitivity are required. The use of automatic control systems in engineering has provided simple, flexible, adjustable and efficient solutions in the steps of theoretical design, realization and application. The sensors, which are small devices for transforming structural changes into electronic signals, play an important role in this field. Specifically humidity sensors are part of industrial routine and daily applications. To determine and control of humidity is a requirement of human comfort and industrial purposes like electronic devices, food storage and textiles etc. [1-5].

The humidity sensing materials can be classified as ceramics or polymers and their working mechanisms could be grouped as capacitive and resistive. However, all the humidity sensors are expected to have high sensitivity. High sensitivity characteristic is necessary to eliminate a number of parts, which are otherwise required to obtain a suitable sensor output. For resistive or ionic type of humidity sensors, humidity sensitivity results from the change of ionic conductivity. The ionic conductivity depends on water absorbtion and desorbtion. Humidity sensitivity characteristic of a sensor is related to intrinsic conductivity of the sensing material and the microstructural features. Chemical absorbtion, physical absorbtion and capillary condensation mechanisms contribute to ionic conductivity of the sensing element [6-9]. The morphology of ceramics influences water vapour absorbtion and desorbtion, especially open porosity has a great effect on the humidity sensitivity of the sensor. Besides, working temperatures at which electrical conductivity under humid environment is measured, affects the conductivity results [10,11].

In the present study, four compositions were prepared with graphite addition as described in the study of Fruth et al.[12]. Following the sintering

* Autor corespondent/*Corresponding author*,
Tel.: +90 533 727 36 08, e-mail: burcuertug@gmail.com

at 1500°C for 2-6h., the electrical conductivity values were measured and transformed into humidity sensitivity values. The effect of porosity percentage on the humidity sensitivity was investigated through several humidity percentages. In order to examine the effect of working temperatures on the humidity sensitivity properties, electrical conductivity tests under humid environment were carried out at 20-80°C.

2.Experimental Procedure

The starting powders used for preparing ceramics were $BaCO_3$ and TiO_2. All compositions included 0.18 wt.% of La_2O_3 to produce n-type semiconducting barium titanate. $BaTiO_3$ compositions were compacted and sintered at 1200-1500°C with 2-6 hours soaking times. Graphite powders were subsequently added to initial powder mixture to form graphite containing barium titanate based compositions. Four different compositions were prepared with 3.5, 4.5, 5.5. and 6.5 wt% compositions and were coded as C-1, C-2, C-3 and C-4, respectively. Grain size of the samples were determined by linear interception method via SEM and and as-sintered porosity values were measured by Archimedes method. Sintered samples were polished and surface-finished before electrical measurements. Electrical conductivity tests for graphite containing compositions were carried out using DC 2-probe method under humid environment. Working temperatures were in the range of 20-80°C and relative humidity range was 20-98%.

3.Results and Discussion

Microstructural images of graphite containing compositions were indicated in Figure 1. The grain sizes of the compositions with various contents were comparable to each other. After the sintering process carried out at 1500°C for 6h., the grain size values obtained for C-4 and C-1 were measured to be 15.7 and 13.3 μm, respectively. Graphite addition increased the average grain size of barium titanate based ceramics. The reason for the enhanced grain growth on graphite addition to pure compositions is the exothermic reactions of graphite powder. On sintering, carbon reacts with oxygen to produce carbon monoxide and carbon dioxide and generates heat to enhance grain growth. However, as graphite addition was raised, carbon accumulates on the grain boundaries to prevent grain growth. Thus as the graphite addition was increased, grain refinement occurred. Graphite addition did not change the microstructural features and grain morphology did not change with graphite addition. As graphite content increased, grain growth was improved in comparison with pure compositions.

Figures 2 and 3, indicate the XRD diagrams of pure barium titanate composition, sintered at 1200°C for 2 and 6h., respectively. As is shown in Figure 2, the symmetry of the atomic structure is no longer cubic but rather tetragonal. Relating to the maximum sintering durations, sintering temperatures below and above the yielded similar patterns with the standard (76-0744) and main phase was observed to be tetragonal $BaTiO_3$. In

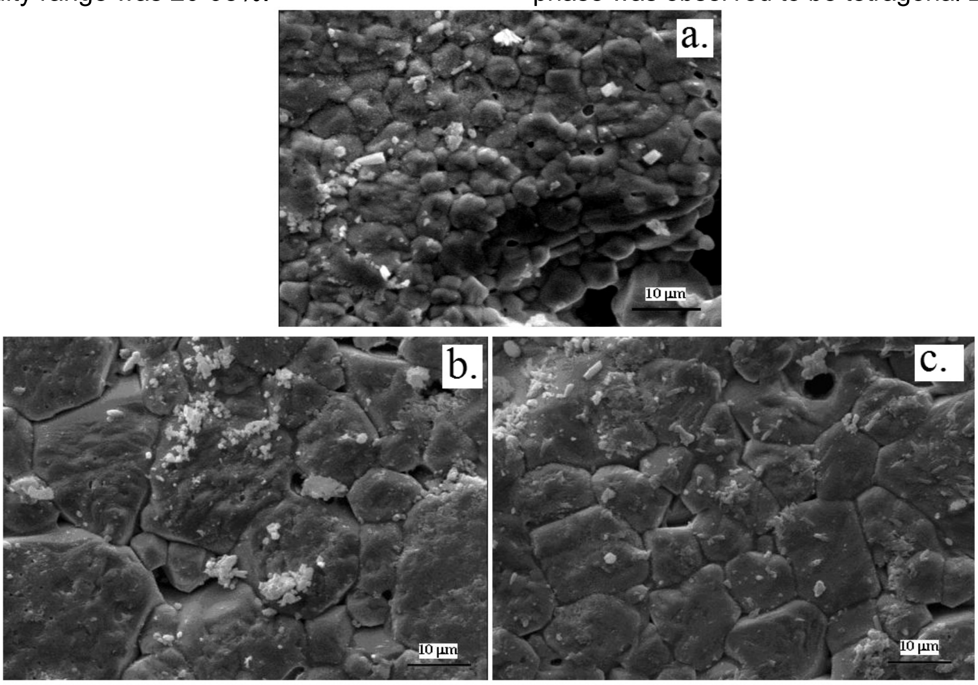

Fig. 1 - SEM images for (a) La-doped, (b) C-1 and (c) C-4 compositions sintered at 1500°C for 6h / *Imagini SEM ale compozițiilor (a) dopată cu La (b) C-1 şi (b) C-4 sinterizate la 1500^{0}C timp de 6 h.*

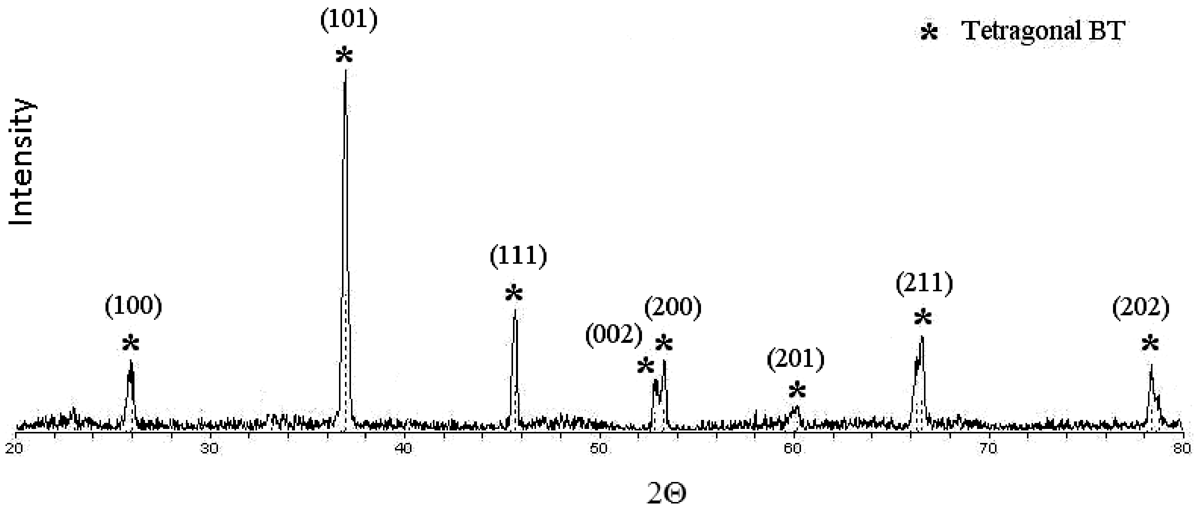

Fig.2 - XRD diagram for La-doped barium titanate sintered at 1300°C for 4h., * denotes tetragonal phase of barium titanate. *Difractograma XRD a litanatului de bariu sinterizat la 1300°C timp de 4 ore. *-faza tetragonală de titanat de bariu.*

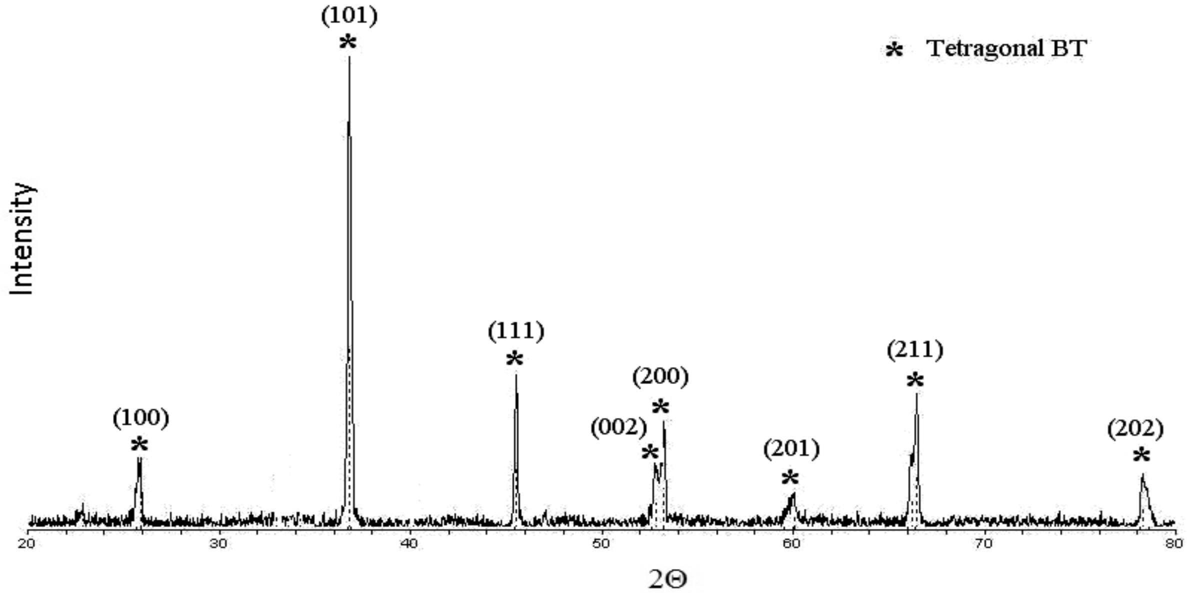

Fig.3. - XRD diagram for graphite added (BTLC-4) barium titanate sintered at 1300°C for 4h., * denotes tetragonal phase of barium titanate / *Difractograma XRD a probei de titanat de bariu şi grafit (BTLC-4) sinterizată la 1300°C timp de 4 ore. *- faza tetragonală de titanat de bariu.*

these patterns, there was no sign of cubic phase and there was a slight difference between the minimum and maximum sintering temperatures.

La_2O_3 doping resulted in grain refinement in comparison to undoped barium titanate as stated in our previous study [13] on sintering in a range of 1200-1500°C. However, grain size value of doped composition was significantly finer than that of graphite containing compositions as explained in [12]. The reason for this was the heat generated by the exothermic reactions occurred on graphite combustion. The grain size of barium titanate ceramics versus sintering time was given in Table 1 for 4 sintering temperatures. For each sintering temperature, the grain size of barium titanate ceramics decreased with increasing graphite content due to graphite accumulation in the grain boundaries. This was valid for each sintering time. The effect of sintering temperature was higly influential regarding the grain growth behaviour of fabricated barium titanate ceramics in a range of 1200-1500°C.

Stable microstructures related to high temperature processes were obtained, as shown in Figure 1, by graphite addition and porosity requirements were satisfied with homogeneous distribution of high porosity percentages throughout the microstructures. In the present study, the application of lower sintering temperatures, i.e. 1200°C, using low amounts of additives, $BaTiO_3$-based ceramics were fabricated to fit long-term room temperature humidity environment applications. Low amount of graphite addition provided the porosity percentages

Table 1

Grain size vs. graphite content variation after sintering at (a) 1200°C, (b) 1300°C, (c) 1400°C and (d) 1500°C for 2-6h.
Variația dimensiunii granulare în funcție de conținutul în grafit după sinterizarea la (a) 1200°C, (b) 1300°C, (c) 1400°C şi (d) 1500°C pentru 2-6h.

a.

Sample code	Grain size (μm) Sintering time		
	2h.	4h.	6h.
BTLC-1	4.7	5.2	5.7
BTLC-2	4.5	4.9	5.4
BTLC-3	4.3	4.7	5.2
BTLC-4	4.1	4.5	5

b.

Sample code	Grain size (μm) Sintering time		
	2h.	4h.	6h.
BTLC-1	6.6	7.3	8
BTLC-2	6.3	6.9	7.6
BTLC-3	5.95	6.5	7.2
BTLC-4	5.6	6.2	6.8

c.

Sample code	Grain size (μm) Sintering time		
	2h.	4h.	6h.
BTLC-1	9.3	10.2	11.2
BTLC-2	8.8	9.6	10.6
BTLC-3	8.3	9.2	10.1
BTLC-4	7.9	8.6	9.5

d.

Sample code	Grain size (μm) Sintering time		
	2h.	4h.	6h.
BTLC-1	13	14.3	15.7
BTLC-2	12.3	13.5	14.9
BTLC-3	11.6	12.8	14.1
BTLC-4	11	12	13.3

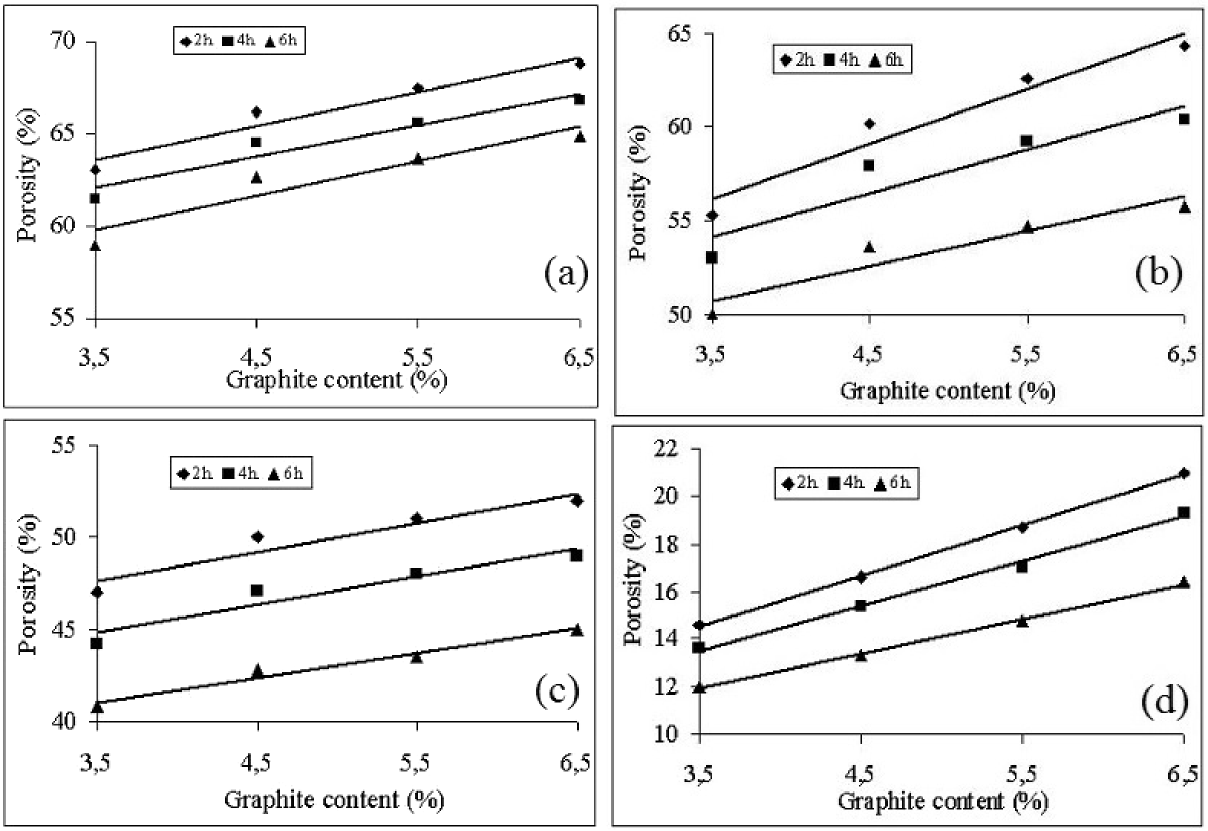

Fig 4 - Porosity vs. graphite content graphs after sintering at (a) 1200°C, (b) 1300°C, (c) 1400°C and (d) 1500°C for 2-6h. / *Variația porozității în funcție de conținutul de grafit după sinterizarea la (a) 1200°C, (b) 1300°C, (c) 1400°C şi (d) 1500°C pentru 2-6h.*

required for humidity sensing process, which is mainly a surface reaction including the adsorption of water vapour to the ceramic surface. The ionic conductivity under humid environment could be maintained by homogeneous distribution of present porosity, especially along the ceramic surface. Thus a combination of sufficient porosity and ionic conductivity enhances the humidity-sensing applications for barium titanate ceramics. Open porosity determined by Archimedes method, which affects electrical conductivity values under humid environment, were shown in Figure 4. Open porosity vs. graphite (pore-forming agent) content curves indicated a linear tendency.

Maximum open porosity obtained by the pore-forming agent was 68.8% and measured for C-4 composition. At lower sintering temperatures, i.e. 1200°C, a tendency to hydration occurred for

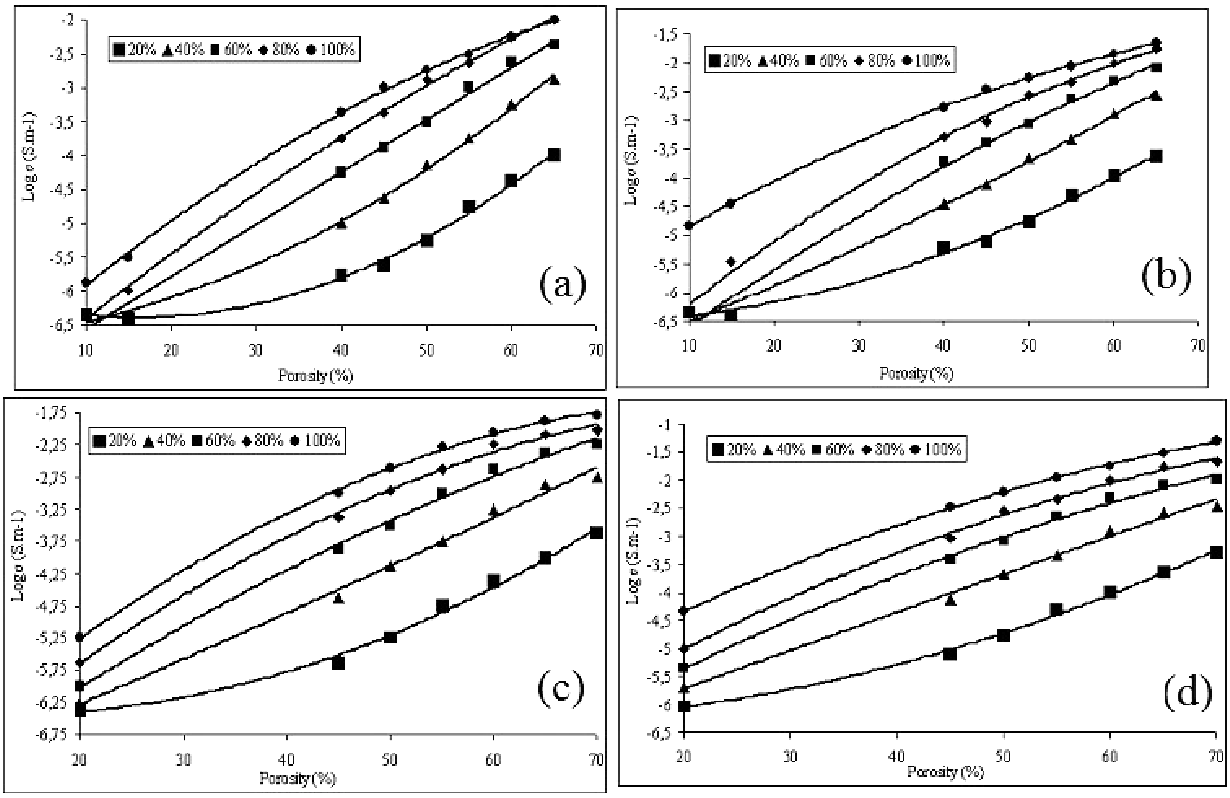

Fig 5 - Electrical conductivity vs. porosity for C-1 at (a) 20°C, (b) 80°C and C-4 (c) 20°C, (d) 80°C / *Variația conductivității electrice în funcție de porozitate pentru probele C-1 la (a)20°C, (b)80°C şi C-4 (c) 20°C, (d)80°C.*

the samples sintered spesifically for 2h. As the sintering time increased to 6h., sintered samples became less porous and stable under humid environment. Maximum porosity value of the samples sintered at 1500°C was 21%. There was a great amount of pore elimination after sintering at 1500°C in a range of 2-6h. The reason for the densification process occurred after 1500°C could be attributed to rapid grain growth kinetics at the particular sintering temperature. It was clear that the effect of sintering duration on the porosity value of sintered barium titanate ceramics was rather limited. Among the parameters which determine the grain growth behaviour of fabricated ceramics, sintering temperature was found to be the dominant parameter.

Regarding the electrical conductivity results, transfer functions in terms of several parameters were evaluated. Electrical conductivity curves given in Figure 5, show that an exponential correlation exists for all graphite added compositions.

First of all, results obtained at room temperature indicated that electrical conductivities increased dramatically with relative humidity range. The conductivity increase resulted due to adsorption process from low relative humidity to high relative humidity. This is due to the adsorption and capillary condensation of water vapour. This leads to increase in the charge carrier, protons in the fabricated ceramic. The porous perovskite-type titanate ceramic was used as humidity sensing material in this study which operate at low temperatures (<100 ºC) as ionic sensor as stated by Viviani et al.[8]. It was reported by Hwang and Choi that the $BaTiO_3$ bulk sample with low density and high resistivity shows large and nearly linear sensitivity to the charged of humidity. He also reported that the microstructure of the sintered body plays a major role in humidity detection [9]. Maximum electrical conductivity measured for C-1 composition at room temperature was 10^{-2} $S.m^{-1}$ and was obtained at 98% of relative humidity due to higher content of condensed water vapour on the surface at this humidity level. At lower relative humidity (20 and 40%), electrical conductivity increased slightly with porosity up to 40%. Above a porosity value of 40%, conductivity increased rapidly to a value of 10^{-4} $S.m^{-1}$ at relative humidity of 20%. This behaviour was also true for the results obtained at 40% of relative humidity and maximum conductivity value was $10^{-2.875}$ $S.m^{-1}$ for this humidity percentage. At both humidity percentage conductivity vs. porosity relationship was exponential. At 60%, electrical conductivity value reached $10^{-2.375}$ $S.m^{-1}$ and porosity dependence became linear and above 60%, conductivity vs. porosity changed to exponential again and then reached maximum value at 98%. At higher humidity percentages, conductivity increased sharply with porosity. Similar to our study, according to Wang et al., $BaTiO_3$ material barium showed a good response to humidity level at room temperature [15].

In order to examine the effect of service temperatures, several conductivity values were measured for 20-80°C. The conductivity values measured at maximum and minimum working temperatures were given for clarity. Figure 5.b shows electrical conductivity vs. porosity measured at 80°C. Maximum conductivity value obtained at 80°C was $10^{-1.65}$ S.m^{-1} and at lower humidity percentages (only 20%), relationship was exponential with a maximum value of $10^{-3.63}$ S.m^{-1}. The initial humidity exposure to the ceramic surface led to rapid conductivity increase. At 40%, relationship was linear with a maximum value of $10^{-2.56}$ S.m^{-1} and above 40%, conductivity increased sharply with porosity indicating an exponential tendency. Maximum value measured at 60% of relative humidity was $10^{-2.09}$ S.m^{-1}. At 80 and 98%, exponential curves reached their maximum values at $10^{-1.76}$ and $10^{-1.65}$ S.m^{-1}, respectively. At 98% of relative humidity, conductivity increased significantly with porosity reaching a value of $10^{-4.84}$ S.m^{-1} for approxiamately 10% of porosity. Electrical conductivity vs. porosity curves for C-4 composition was given in Figure 5.c. As can be seen from the relationship curve, conductivity increased with graphite content reaching its maximum at C-4 composition with a value of $10^{-1.78}$ S.m^{-1}. The conductivity of C-4 was greater than that of C-1 composition by the order of one. Except 20 and 40% of relative humidity, of which maximum values were $10^{-3.625}$ and $10^{-2.75}$ S.m^{-1}, respectively, conductivity vs. porosity curves were exponential.

At 60 and 80% of relative humidity, maximum values were $10^{-2.25}$ and $10^{-2.02}$ S.m^{-1}, respectively and at 40% conductivity vs. porosity curve was linear. When working temperature was raised to 80°C, maximum electrical conductivity was $10^{-1.3}$ S.m^{-1} for C-4 composition. Minimum conductivity value was $10^{-3.29}$ S.m^{-1} at 80°C. At 40% of relative humidity, maximum value was measured to be $10^{-2.45}$ S.m^{-1} and conductivity vs. porosity relationship was linear. Exponential curves obtained at 60 and 80% reached their maximum at $10^{-1.98}$ and $10^{-1.67}$ S.m^{-1}, respectively.

Besides conductivity vs. porosity curves, humidity sensitivity characteristic was shown as a function of porosity in Figure 6. It was clear that humidity sensitivity increased dramatically with porosity. This is due to water vapour adsorption to the surface of the barium titanate ceramic and capillary condensation in the porosity in the ceramic. Adsorption is an exothermic process, whereas desorption needs external energy for water molecules to depart from film surface [16]. Therefore, rapid humidity sensitivity increase seems to be the result of high porosity.

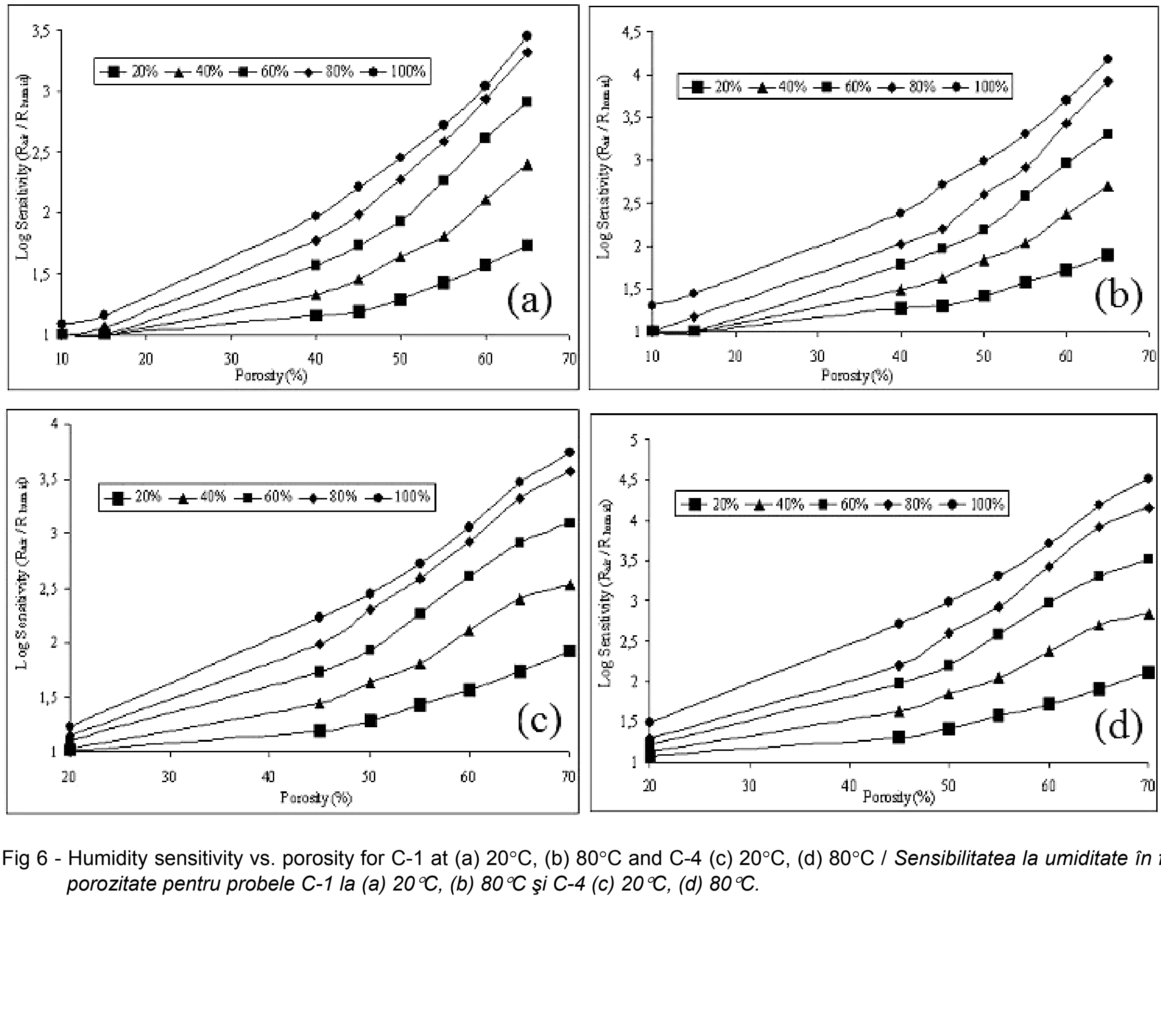

Fig 6 - Humidity sensitivity vs. porosity for C-1 at (a) 20°C, (b) 80°C and C-4 (c) 20°C, (d) 80°C / *Sensibilitatea la umiditate în funcție de porozitate pentru probele C-1 la (a) 20°C, (b) 80°C şi C-4 (c) 20°C, (d) 80°C.*

At lower porosity percentages, humidity sensitivity values obtained at different humidity percentages were comparable to each other. However, as porosity increased humidity sensitivity values at various humidity levels differentiated. For C-1 composition maximum humidity sensitivity values were 3.45 and 4.18 at 20 and 80°C, respectively. Humidity sensitivity curves of C-1 indicated a sharper increase than those of C-4 composition especially at higher porosity and humidity percentages. Maximum sensitivity values for C-4 composition were measured to be 3.74 and 4.51 at 20 and 80°C, respectively. The results indicated above show that the ceramic conductivity for all humidity levels increases with an increase in temperature. The temperature increase enhances the conductivity of the barium titanate. This is due to the fast moving electrons in the fabricated ceramic. This leads to high conductivity. The conductivity increase by the temperature is limited in comparison to the humidity effect. It was concluded that porosity and working temperatures had a noticable effect on the electrical conductivity and humidity sensitivity properties of barium titanate based porous ceramics.

4.Conclusion

The effects of graphite additions on the porosity and electrical conductivity of porous barium titanate ceramics were investigated. The effects of the amount of pore-forming agent on the porosity and microstructural features of $BaTiO_3$ based ceramics were examined. Graphite addition resulted in a slight grain refinement for all the compositions studied. Porosity percentage variations depending on the content of the pore-forming agent could be evaluated as a strong parameter to affect electrical conductivity under humid environment. As the working temperature was raised, conductivity and sensitivity characteristics increased noticeably. It was concluded that porosity and working temperatures affected the humidity sensitivity characteristic of barium titanate ceramics.

REFERENCES

1. J. Fraden, Handbook Of Modern Sensors: Physics, Designs and Applications, Birkhauser, 2004, 1.
2. I. Sinclair, Sensors and Transducers, Newnes, 2001, 170.
3. G. Tschulena and A. Lahrmann, Sensors Applications, Sensors in Household Appliances, John Wiley and Sons 2003, 5.
4. B.R. Eggins, Chemical Sensors and Biosensors, John Wiley and Sons 2002, 2.
5. F.G. Barth, J.A.C. Humphrey and T.W. Secomb, Sensors and Sensing in Biology and Engineering, Birkhauser, 2003, 20.
6. G. Sberveglieri, 'Gas Sensors: Principles, Operation and Developments', Springer 1992, 365.
7. A. Rae, M.Chu and V. Ganine, Barium titanate – Past,. 1. present and future, Ceram.Trans., 1999, **100**, 1.
8. M. Viviani, M.T. Buscaglia, V. Buscaglia, M.Leoni, and P. Nanni, Barium perovskites as humidity sensing materials, J. of the European Ceramic Society, 2001, **21**, 1981.
9. T.J. Hwang, and G.M. Choi, Electrical characterization of porous $BaTiO_3$ using impedance spectroscopy in humid condition, Sensor and Actuators B, 1997, **40**, 187.
10. K. Park, Characteristics *of* porous *$BaTiO_3$*- based PTC thermistors fabricated *by* adding graphite powders, Materials Science and Engineering B, 2004, **107**, 19.
11. K. Park and D.J. Seo, Gas sensing characteristics of BaTi03-based ceramics, Materials Chemistry and Physics, 2004, **85**, 47.
12. V. Fruth, C. Andronescu, C. Hornoiu, E. Tenea, A. Rusu, and R. Scurtu, Processing Of(La, Sr)(Ga, Mg)O3 Solid Electrolyte Using An Enhanced Solid State Technique, Revista Romana de Materiale, 2011, **41**, 56.
13. B. Ertug, Electrical Conductivity and Hysteresis Characteristic of $BaTiO_3$-Based Sensors with Polymethyl metacrylate (PMMA) Pore Former, Sensors and Materials, 2013, **25**, 309.
14. J.Wang, H.Wan, and Q.Lin, Properties of a nanocrystalline barium titanate on silicon humidity sensor, Meas, Sci. Technology, 2003, **14**, 172.
15. E.Traversa, Y.Sadaoka, M.C. Carotta, and G. Martinelli, Environmental monitoring field tests using screen-printed thick-film sensors based on semiconducting oxides, Sensors and Actuators B, 2000, **65**, 181.

****