











already revealed by XRD and DTA/TG measurements. The samples which exhibit the lowest activation energy is associated the structure characterized by the fluorite type fcc lattice is likely responsible for opening of migration pathways for the oxide ions, and consequently to a decreasing of the activation energy.

The main purpose of this study is to find an electrolyte which does not have any degradation in its properties with time; this maybe caused either interaction between different electrochemical cell materials or by instability of the ionic conductor under operation conditions. So this sample has been firstly heated from room temperature to 650, 700, 750 and 800 °C in 48 hours and cooled from this temperature to room temperature in the same time. After this process, the four-point probe conductivity measurements have been performed.

Figure 5 shows the hysteresis curve obtained for the sample A6. This sample has been firstly heated from room temperature to 800 °C in 2 hours and cooled from this temperature to room temperature within the 4 hour s. During this process, the four-point probe conductivity measurements have been performed. The hysteresis curve was occurred for this sample due to time interval difference of heating/cooling processes. From this figure, the slopes of these curves nearly are the same. It means that there is no gradation in the physical and chemical properties of this sample after applying the operation condition.

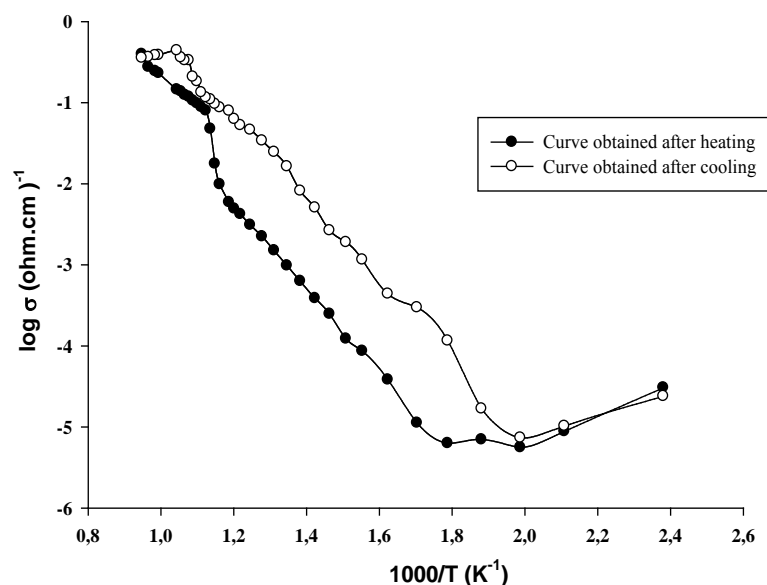


Fig. 5. Conductivity hysteresis curve obtained for the sample A6 obtained approximately 5 hours being heated from room temperature to 800 °C and cooled to room temperature

TG/DTA measurements of the samples have been carried out after the conductivity measurements of the samples using the same pellets. In figure 6, TG/DTA graphics of the sample A6 annealed at 750 °C and for 48 hours are given. From this figure, a wide range of exothermic peak is seen in a temperature range between 325-415 °C for A6 sample in DTA curve. Similar variation is seen between the same temperature ranges in TGA curve whose slope is changing during heating treatment. In this case, this peak results from the order/disorder transformation in the structure of the sample rather than the phase transformation. During the cooling process, there are no exothermic peak and slope changes because of long cooling time interval. This transformation is seen in the conductivity graphics of the same sample and its hysteresis curve (Fig. 5) too.

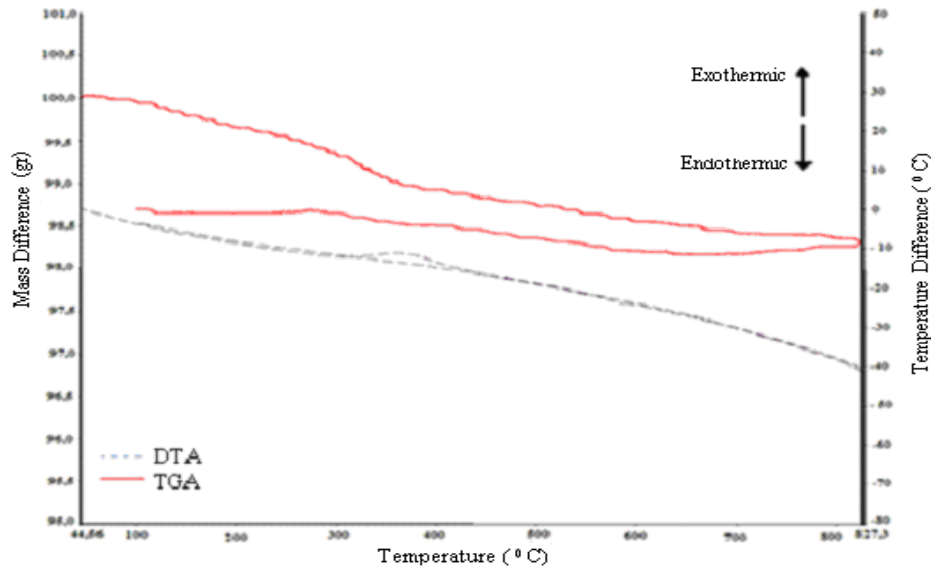


Fig. 6. TG/DTA graphics of sample A6 developed at 750 °C and for 48 hours

#### 4. Conclusion

In this work, data obtained from XRD, DTA, TGA and four probe point method measurements for  $(\text{Bi}_2\text{O}_3)_{1-x-y}(\text{Ho}_2\text{O}_3)_x(\text{Dy}_2\text{O}_3)_y$  ( $x=1, 3, 5, 7, 9, 11$  mol%,  $y=11, 9, 7, 5, 3, 1$  mol %) ternary system samples synthesized at different temperatures by solid state reaction method has been investigated in detail and some important results have been obtained for the chosen sample A6 as following:

- According to the obtained XRD results, all the samples synthesized at 700 °C, 750 °C and 800 °C for 48 hours have dominantly homogeneous face centered cubic  $\delta\text{-Bi}_2\text{O}_3$  phase. The samples annealed at 650 °C have mixed phases composed from monoclinic  $\alpha\text{-Bi}_2\text{O}_3$  phase and fcc  $\delta\text{-Bi}_2\text{O}_3$  phase.
- According to conductivity measurements, all the samples, having stable  $\delta\text{-Bi}_2\text{O}_3$  phase and synthesized at 700 °C, 750 °C, and 800 °C for 48 hours, have a good oxygen ion conductivity property.
- It has been observed that the electrical conductivity of all the samples increases while the percentage of the  $\text{Ho}_2\text{O}_3$  doping materials increases.
- The best electrical conductivity has been observed for the sample A6 synthesized at 750 °C for 48 hours and having doping ratios % 11 mol for  $\text{Ho}_2\text{O}_3$  and % 1 mol for  $\text{Dy}_2\text{O}_3$  and maximum conductivity value has been measured as  $6.11 \times 10^{-1} (\Omega \cdot \text{cm})^{-1}$ .
- Stable  $\delta$ -phase of  $(\text{Bi}_2\text{O}_3)_{1-x-y}(\text{Ho}_2\text{O}_3)_x(\text{Dy}_2\text{O}_3)_y$  ternary system has been observed firstly in this study in operation conditions of an SOFC.

#### Comment

We are planning to perform resistance tests for this material for long time periods under the operation conditions to show that this material can be used as an electrolyte in SOFCs.

#### References

- [1] D. Music, S. Konstantinidis and J. M. Schneider, Equilibrium structure of  $\delta\text{-Bi}_2\text{O}_3$  from first principle, J. Phys.: Condens. Matter, 21, 2009, 175403-175480.

- [2] C. -Y. Hsieh, K.-Z. Fung, Crystal structure and electrical conductivity of cubic fluorite-based  $(\text{YO}_{1.5})_x(\text{WO}_3)_{0.15}(\text{BiO}_{1.5})_{0.85-x}$  ( $0 \leq x \leq 0.4$ ) solid solutions, *J. Solid State Electrochem*, 13, 2009, 951-957.
- [3] P.K. Cheekatamarla, M. F. Caine, and J. Cai, Internal reforming of hydrocarbon fuels in tubular solid oxide fuel cells, *International Journal of Hydrogen Energy*, 33, 2008, 1853-1858.
- [4] S.R Xiao-Feng Ye, Z.R Wang, L. Wang, X.F Xiong, T.L. Sun Wen, Use of a catalyst layer for anode-supported SOFCs running on ethanol fuel, *Journal of Power Sources*, 177, 2008, 419-425.
- [5] M. Wang, and K. Woo, Impact of  $\text{Sr}_2\text{MnO}_4$  preparation process on its electrical resistivity, *Energy Conversion and Management*, 49, 2008, 2409–2412.
- [6] S.H. Jung, E.D. Wachsman and N. Jiang, Structural Stability and Conductivity of Cubic  $(\text{WO}_3)_x-(\text{Dy}_2\text{O}_3)_y-(\text{Bi}_2\text{O}_3)_{1-x-y}$ , *International Journal of Ionics*, Volume 8, Numbers 3-4, 2002, 210-214.
- [7] M. Benkaddour, M.C. Steil, M. Drache, and P. Conflant, The Influence of Particle Size on Sintering and Conductivity of  $\text{Bi}_{0.85}\text{Pr}_{0.105}\text{V}_{0.045}\text{O}_{1.545}$  Ceramics, *Journal of Solid State Chemistry*, 155, 2000, 273-279 .
- [8] N.M. Sammes, G.A. Tompsett, H. Nafe and F. Aldinger, Bismuth based oxide electrolytes structure and ionic conductivity, *Journal of European Ceramic Society*, 19, 1999, 1801-1826.
- [9] N. Jiang, E.D. Wachsman and S.H. Jung, A higher conductivity  $\text{Bi}_2\text{O}_3$ -based electrolyte, *Solid State ionics*, 150, 3-4, 2002, 347-353.
- [10] H.A. Harwing, On the Structure of Bismuthsesquioxide: The  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ -phase, *Z. Anorg. Allg. Chem.*, 444, 1978, 151-166.
- [11] A. Watanabe, Is it possible to stabilize  $\delta\text{-Bi}_2\text{O}_3$  by an oxide additive?, *Solid State Ionics*, 40-41, 1990, 889-892 .
- [12] N. Jiang, R.M. Buchanan, F.E.G. Henn. A.F. Marshall, D.A. Stevenson, E.E. Wachsman, Aging phenomenon of stabilized bismuth oxides, *Mater. Res. Bull.*, 29, 1994, 247-254.
- [13] E.D. Wachsman, S. Boyapati, M.J. Kaufman, N. Jiang, Modeling of Ordered Structures of Phase-Stabilized Cubic Bismuth Oxides, *J. Am. Ceram. Soc.*, 83, 2000, 1964-1968.
- [14] E.D. Wachsman, G.R. Ball, N. Jiang and D.A. Stevenson, Structural and defect studies in solid oxide electrolytes, *Solid State Ionics*, 52, 1992, 213-218.
- [15] S. Boyabati, E.D. Wachsman and B.C. Chakoumakos, Neutron diffraction study of occupancy and positional oxygen ions in phase-stabilized cubic bismuth oxides, *Solid state Ionics*, 138, 2001, 293-304.