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Investigation of electrical, structural and thermal stability properties of $(Bi_2O_3)_{1-x-y}(Dy_2O_3)_x(Ho_2O_3)_y$ ternary system

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Keywords
Electrolyte, Solid state reaction, Fuel cell, Electrical conductivity, Four-probe point method

ABSTRACT

The aim 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 the different electrochemical cell materials or by instability of the ionic conductor under operation conditions. Accordingly, this $(Bi_2O_3)_{1-x-y}(Ho_2O_3)_x(Dy_2O_3)_y$ ternary system (x=11, 12, 13, 14 mol % and y=4, 3, 2, 1 mol %, dopant concentrations) sample materials were synthesized using solid state reaction method sintering each of them at 750°C for 48 hours. Structural, electrical and thermal properties of the samples which are candidate of electrolyte for solid oxide fuel cells have been evaluated by means of X-ray diffraction (XRD), four-probe method, and thermal analysis (TG / DTA). XRD measurements showed that all of the samples have stable *δ*- type phase which was also supported by the TG / DTA measurements.

$(Bi_2O_3)_{1-x-y}(Dy_2O_3)_x(Ho_2O_3)_y$ üçlü sistemin elektriksel, yapı ve termal kararlılık özelliklerinin incelenmesi

Anahtar Kelimeler
Katıhal reaksiyonu, Yakıt hücresi, Elektriksel iletkenlik, Dört-nokta metod

ÖZET

Bu çalışmanın amacı; zamanla özellikleri bozulmayan ve çalışma şartları altında iyonik iletkenliğini koruyan elektrolit/elektrolitler tespit etmektir. Bu doğrultuda, $(Bi_2O_3)_{1-x-y}(Ho_2O_3)_x(Dy_2O_3)_y$ üçlü sistemin (x=%11, 12, 13, 14 mol ve y=% 4, 3, 2, 1 mol, katkı konsantrasyonu) numuneleri katıhal reaksiyonu ile 48 saat 750°C ısıl işleme tabi tutularak hazırlandı. Katı Oksit Yakıt Hücresi (SOFC) için en iyi katı elektrolit özelliklere sahip olabilecek numunelerin yapısal özellikleri X-ışınları difraktometresi (XRD), elektriksel özellikleri dört-nokta metodu ve termal özellikleri diferansiyel termal analiz (TG / DTA) ölçüm sistemleri ile ölçüldü. XRD ölçümleri 48 saat 750°C ısıl işlem sonucunda bütün numuneler δ- Bi_2O_3 fazında kararlı olduğunu gösterdi.

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1. Introduction

Recently, it has been known that bismuth oxide based and doped with the other two ceramic oxides are ternary materials with the properties showing promise of utility in solid oxide fuel cells SOFC's [1-7]. In addition, the need to develop oxide ion conductive materials with high conductivity and desired structure stability at low temperature directs most of the research toward solid oxide electrolyte materials. Among these electrolyte materials, Bi_2O_3 - based solid oxide electrolyte materials with δ-phase fcc fluorite type crystal structure are of interest for use in solid oxide fuel cell (SOFC) due to their high oxide ion conductivity [8,9]. The fluorite type phase of pure Bi_2O_3, known as the most highly conductive oxide-ion conductor, has a conductivity of about 1 Scm^{-1} at 750 °C. But, δ-phase Bi_2O_3 is stable only between 730 °C and 825 °C and cannot be quenched to room temperature [10]. However, the δ-phase can be obtained at room temperature by doping with some transition metal (Nb, Ta, V and W) and rare earth (Sm-Lu). It is also possible to use combination of oxides, so called double doping, to obtain the δ fluorite type phase. Fluorite type δ–phase materials display very high oxide ion conductivity which is attributed to the highly polarisable Bi^{3+} cations and highly disordered structure of sublattice [11-15]. Structural and conductive properties of a solid material during the various temperature ranges determine its suitability as an electrolyte in the practical use. If an electrolyte material has a high conductive behavior over a long period of time at reasonably low temperature, it is possible to use at operation of a SOFC. Many researchers were reported that the fluorite type δ–phase Bi_2O_3 cannot be stabilized [11-13]. Some these kinds of materials had completely transformed into mixture phases after annealing for long time period. In addition, the conductivity decay can also occur for the fluorite type materials without changing its structure. The rate of conductivity decay is dependent on annealing temperature, long ordering oxide-ion sublattice and amount of doped cations. The aim 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 the different electrochemical cell materials or by instability of the ionic conductor under operation conditions.

2. Experimental

2.1. Sample preparation

We have tried to stabilize the fluorite type δ-phase in the ternary system $(Bi_2O_3)_{1-x-y}(Dy_2O_3)_x(Ho_2O_3)_y$. As a result, we could obtained a stabilized δ-phase in limited compositional range of x and y.

The desired proportions of the samples were accurately weighed and thoroughly mixed. The mixture was heated in an alumina crucible at 750 °C for 48 h. Next, the samples were examined by X-ray diffraction XRD using CuKα radiation. Then, the prepared pellets were annealed at 750 °C for 48 h. Finally, thermal behavior of the samples was taken the differential thermal analysis (DTA) measurements in order to find out whether any phase transition exists or not, after each measurement.

2.2. XRD measurements

Powder XRD measurements is carried out by using Bruker AXS D8 Advance type diffractometer with an interval $2\Theta = 10^o–90^o$, scanning $0{,}002^o$/min, and Cu-Kα radiation for the determination of the crystal structure of the samples at room temperature. These measurements were repeated for the powders of the samples obtained after every sintering process. Then, Diffrac Plus Eva packet program was used to analyze the unit lattice cell parameters (a, b, c, α, β, γ), Miller indexes, and the distance between the layers, d. On the other hand, Win-Index Professional Powder Indexing packet program was used for the indexing of the diffraction peaks in the powder patterns of the samples.

2.3 Electrical measurements

Conductivity of the samples was measured using four-point probe method. The pellets of the samples with 13 mm diameter and 2 mm thick were obtained by using a conventional press and then the pellets were being air-quenched after sintering. All of the measurements in this work were carried out by means of Data Acquisition Control System associated with a PC, interface card IEEE-488.2, multimeter with scanning card (Keithley 2700, 7700-2), programmable power supply (Keithley 2400), and computer program written for this

purpose. These measurements were repeated for several times because of the electrical conductivity measurements performed during the first heating process are not enough to represent the complete electrical behavior of the samples.

2.4. TG/DTA measurements

The thermal behavior of the annealed materials was investigated by TG / DTA by means of DIAMOND TG/DTA-PERKIN ALMER Marck system. The samples whose masses are about 20-50 mg were heated at 200 °C min^{-1} in an alumina crucible and cooled quickly to room temperature under a stream of air.

3. Results and discussion

3.1. XRD measurement results

Figure 1 shows the comparisons of the XRD spectra of the samples annealed at 750 °C for 48 hours. From this figure, it is observed that all the samples have only δ-phase.

There is no transformation of the quenched δ-phase is evidenced on the XRD patterns. The fluorite type δ-phase is obtained at the end of the process. The first generated δ-phase has been kept stable during the electrical measurement for all the samples.

Summary of the observed phases from XRD measurements of the $(Bi_2O_3)_{1-x-y}(Ho_2O_3)_x(Dy_2O_3)_y$ ternary-systems with different dopant ratios is given in Table 1. As seen from this table, all the samples have stable fcc δ-phase.

Table 1. Observed phases for $(Bi_2O_3)_{1-x-y}(Ho_2O_3)_x(Dy_2O_3)_y$ ternary-systems with different dopant ratios

Synthesing temperature (°C)	Synthesing time (hour)	$(Ho_2O_3)_x(Dy_2O_3)_y(Bi_2O_3)_{1-x-y}$ (*x,y = mol %*)			
		x=11 y=4	x=12 y=3	x=13 y=2	x=14 y=1
750	100	A1 **δ**	A2 **δ**	A3 **δ**	A4 **δ**

3.2 Electrical conductivity measurements

The conductivity measurements were performed on the samples ($(Bi_2O_3)_{1-x-y}(Ho_2O_3)_x(Dy_2O_3)_y$) ternary system (x=11, 12, 13, 14 mol % and y=4 , 3 , 2 , 1 mol %). Conductivity measurements were only carried out up to 850 °C in order to ensure that melting does not occur. The conductivity of this sample is ~0.3 $(\Omega.cm)^{-1}$ placing it among the most highly conductive materials known.

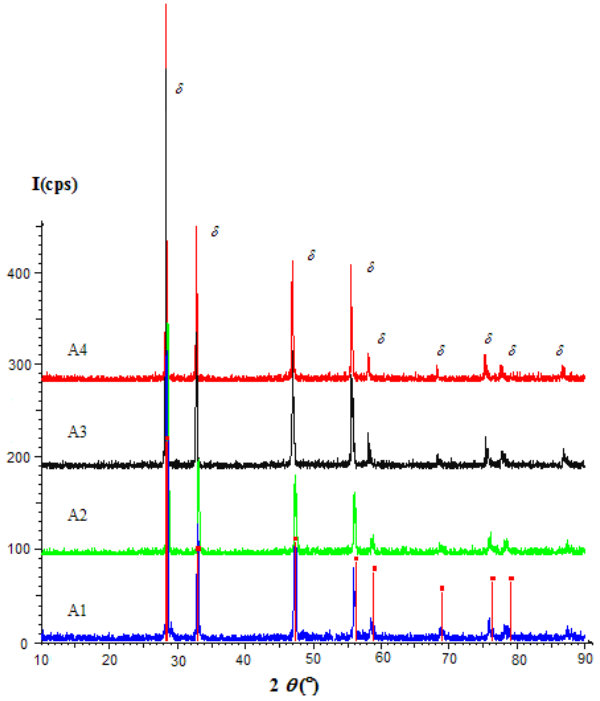

Fig. 1. Comparisons of the XRD spectra of the samples annealed at 750 °C and for 48 hours and having fcc δ-Bi_2O_3 phase A1, A2, A3, A4

Figure 2 shows the graphics of the conductivity of the samples versus to (1000/T) ^oC. As seen from this figure, all the curves are similar with each other. It is the expected result since all of them have stable fcc δ-phase. These results were supported by the XRD patterns of the samples which have been given in Fig.1 too. As seen from this figure, two distinct regions observed on the curves corresponding to an order-disorder δ-phase transition which exhibits similar activation energy at these two regions. The characteristics of the conductivity curves are similar for all the samples. Activation energies of the samples can be obtained from the Arrhenius equation. As mentioned previously two distinct regions are observed for all samples corresponding to an order-disorder δ-phase transition which exhibits similar activation energy at these two regions. Activation energy calculated for sample A1, A2, A3 ve A4 corresponding to the high temperature region is found 0.52, 0.64 , 0.52 and 0.52 eV, respectively. Also, the conductivity results are in

good agreement with these already revealed by XRD and DTA measurements.

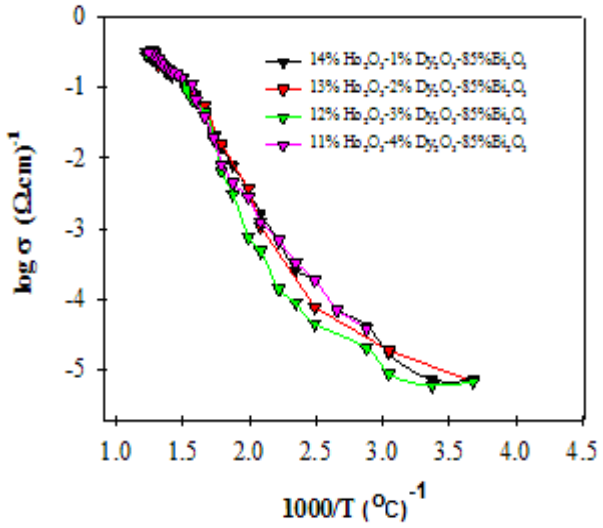

Fig. 2. Oxygen conductivity, as a function of temperature, for the samples A1, A2, A3, A4 obtained at 750 °C for 48 hours

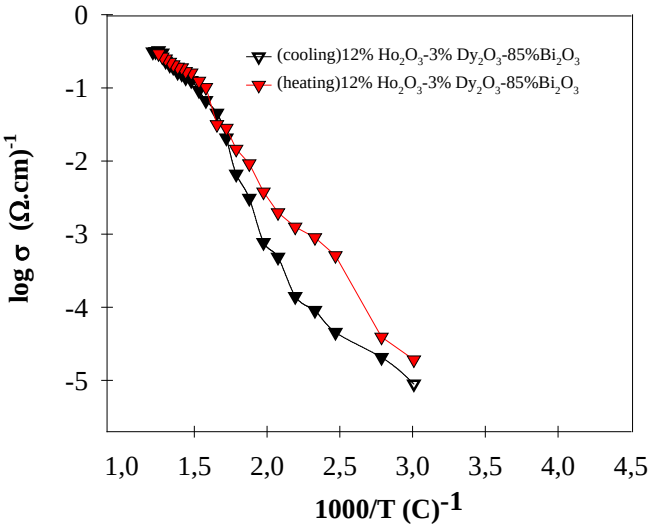

Fig. 3. Conductivity hysteresis curve obtained for the sample A2 obtained approximately 5 hours being heated from room temperature to 850 °C and cooled to room temperature.

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 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 3 shows the hysteresis curve obtained for the sample A2. This sample has been firstly heated from room temperature to 850 °C in 2 hours and cooled from this temperature to room temperature within the 4 hours. 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.

TG/DTA measurements of the samples have been carried out after the conductivity measurements of the samples using the same pellets. During the cooling and heating process, there are no exothermic peak and slope changes because of long cooling time interval (Fig. 4). This transformation is seen in the conductivity graphics of the same sample and its hysteresis curve (Fig. 3) too.

4. Conclusion

In this work, data obtained from XRD, TG/ DTA, and four probe point method measurements for $((Bi_2O_3)_{1-x-y}\ (Ho_2O_3)_x(Dy_2O_3)_y)$ (x=11, 12, 13, 14 mol % and y=4, 3, 2, 1 mol %) ternary system samples synthesized by solid state reaction method has been investigated in detail and some important results have been obtained for the chosen sample A4 as following:

- According to the obtained XRD results, all the samples synthesized at 750 °C for 48 hours have homogeneous face centered cubic δ-Bi_2O_3 phase.
- According to conductivity measurements, all the samples, having stable δ-Bi_2O_3 phase and synthesized at 750 °C for 48 hours, have a good oxygen ion conductivity property.

- It has been observed that the electrical conductivity of all the samples parallel while the percentage of the Ho_2O_3 doping materials increases (the percentage of the Dy_2O_3 doping materials decreases).
- Stable δ-phase of $(Bi_2O_3)_{1-x-y}(Ho_2O_3)_x(Dy_2O_3)_y$ ternary system has been observed firstly in this study in operation conditions of an SOFC.

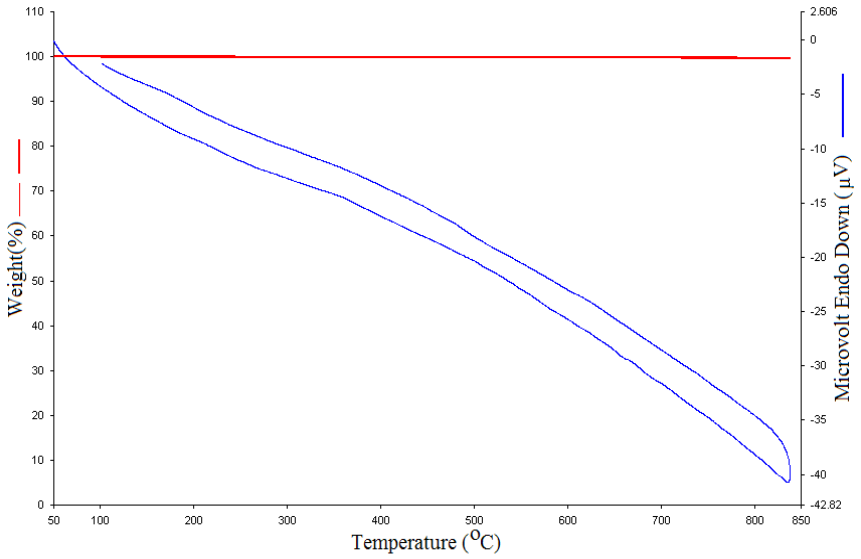

Fig. 4. TG/DTA graphics of sample A1 developed at 750 °C and for 48 hours

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