

PHASE STABILITY AND CONDUCTIVITY OF δ -Bi₂O₃ WITH MIXTURE OF YTTRIUM AND YTTERBIUM OXIDES

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Abstract In this research Bi₂O₃ was doped with mixtures of 8, 10, 12 and 18 mol% of Y₂O₃ and Yb₂O₃ in order to stabilize the δ -Bi₂O₃ phase using solid state reaction technique. Experimental samples were fabricated by isostatic pressing and sintering at 850°C for 24 h. X-ray diffraction analysis detected cubic phase (δ -Bi₂O₃) as the sole stable crystalline phase in samples including 12 and 18 mol% of Y₂O₃ and Yb₂O₃. The tetragonal phase was also observed in samples with 8 and 10% mol additives. X-ray diffraction analyses on aged samples at 600 °C with 12 mol% additives revealed that the δ -Bi₂O₃ phase was transformed to the tetragonal polymorph form. Results of ionic conductivity measurements showed that samples with 12 mol% additives (88 mol% Bi₂O₃, 8 mol% Y₂O₃ and 4 mol% Yb₂O₃) had a higher ionic conductivity than the other samples.

Keywords Powders-solid state reaction; X-ray methods; Electrical conductivity; Bismuth oxide; Fuel cells.

چکیده در این تحقیق به منظور پایدار نمودن فاز مکعبی (δ -Bi₂O₃)، اکسید بیسموت با مقادیر مختلف ۸، ۱۰، ۱۲ و ۱۸ درصد مولی افزودنی همزمان دو اکسید ایتریوم و ایتربیوم و به روش حالت جامد آلاینده شد. نمونه‌های مورد نظر به کمک پرس ایزواستاتیک شکل داده شده و سپس در دمای ۸۵۰ °C به مدت ۲۴ ساعت تفجوشی شدند. آنالیز پراش پرتو ایکس نشان داد که نمونه‌های حاوی ۱۲ و ۱۸ درصد مولی اکسید ایتریوم و ایتربیوم شامل تک فاز مکعبی (δ -Bi₂O₃) بوده و نمونه‌های حاوی ۸ و ۱۰ درصد مولی اکسید ایتریوم و ایتربیوم شامل فاز تتراگونال می‌باشد. همچنین، بررسی اثر فرآیند پیرسازی روی نمونه‌ها در دمای ۶۰۰ °C نشان داد که پس از گذشت زمان، فاز مکعبی به تتراگونال تبدیل می‌شود. نتایج حاصل از اندازه‌گیری هدایت یونی نمونه‌ها نیز نشان داد که نمونه‌های حاوی ۱۲ درصد مولی افزودنی (۸۸ درصد مولی اکسید بیسموت با ۸ درصد مولی اکسید ایتریوم و ۴ درصد مولی اکسید ایتربیوم) بالاترین مقدار هدایت یونی را دارا می‌باشد.

1. INTRODUCTION

Bismuth oxide has two different stable crystallographic polymorphs. The cubic phase (δ -Bi₂O₃) of bismuth oxide is stable between 730-825°C and its transformation monoclinic structure forms below 730°C. In addition to these phases, two intermediate metastable phases namely β -Bi₂O₃ (tetragonal) and α -Bi₂O₃ (bcc) are known to exist at about 650°C [1-5].

The cubic phase of bismuth oxide with a fluorite structure has high ionic conductivity due to the presence of 25% oxygen vacancies in its structure; therefore, bismuth oxide has the potential to be used as an oxygen pump, oxygen sensor and as a fuel cell electrolyte [1-4, 6-8]. The δ phase, however, transforms to the low

temperature monoclinic phase during cooling and the volume change accompanying the transformation leads to disintegration of the sample [1-3, 9-10]. Thus, from an applications standpoint, it is necessary to stabilize the cubic phase of Bi₂O₃ with the addition of other oxides.

It is known that addition of alio or iso valent ions such as Y₂O₃, several rare earth oxides or alkaline earth oxides can stabilize the cubic phase at lower temperature [1-5, 7-8]. It has also been shown that the δ phase with two rare-earth oxide dopants could be stabilized down to room temperature, with much lower content of double oxides than that of a single oxide [9]. This comparative effect was attributed to the increase in entropy of the resulting ternary system as a consequence of mixing [10, 11].

In this study we stabilized δ -Bi₂O₃ at room temperature by using a mixture of two oxides (Y₂O₃ and Yb₂O₃). Then the stability of δ phase was investigated for different aging times and the corresponding ionic conductivity of the samples was measured.

2. EXPERIMENTAL PROCEDURE

Bismuth Oxide (Extra pure, Merck), Y₂O₃ (99.99%, Alfa Aesar) and Yb₂O₃ (99.99%, Alfa Aesar) were used as raw materials and Ethylene glycol as binder for die pressing.

Powders were weighed in desired proportions as listed in Table 1 and mixed in acetone using 24 h milling in a polyethylene jar. The powder mixture was dried and compacted into disk shaped pellets measuring 1mm in thickness and 13mm in diameter using uniaxial die pressing, followed by isostatic pressing at 1850 bar. Samples were placed in an alumina crucible, covered with alumina cap to minimize loss of Bi₂O₃ by volatilization, and then sintered in air at 850°C for 24h. Samples were usually quenched to room temperature by removing from the furnace at high temperature. Phase analyses were carried out by X-ray diffraction (Philips PW1310) using CuK α radiation with a Ni filter at 2 θ =20-60° stepping 0.01 degrees every 6 sec.

TABLE 1. Composition of samples

Sample Code	Bi ₂ O ₃ (mol%)	Y ₂ O ₃ (mol%)	Yb ₂ O ₃ (mol%)
Bi _{0.88} Y _{0.06} Yb _{0.06} O _{1.5}	88	6	6
Bi _{0.88} Y _{0.08} Yb _{0.04} O _{1.5}	88	8	4
Bi _{0.88} Y _{0.04} Yb _{0.08} O _{1.5}	88	4	8
Bi _{0.02} Y _{0.09} Yb _{0.09} O _{1.5}	82	9	9
Bi _{0.82} Y _{0.06} Yb _{0.12} O _{1.5}	82	6	12
Bi _{0.82} Y _{0.12} Yb _{0.06} O _{1.5}	82	12	6
Bi _{0.9} Y _{0.05} Yb _{0.05} O _{1.5}	90	5	5
Bi _{0.92} Y _{0.04} Yb _{0.04} O _{1.5}	92	4	4

Also, for investigation on the effect of aging, some of the sintered samples, including 12 mol% co-dopants (Y₂O₃ and Yb₂O₃), were placed in a furnace at 600°C for 72 to 352 h; then the crystalline phase of the samples for different periods of aging were analyzed by X-ray diffraction.

Impedance spectra of the selected samples were measured in air using a FRA Auto Lab Impedance

Analyzer. Impedance was measured on disk shaped samples. Both sides of samples were coated with platinum paste which formed a circular thin disk with diameter of 1cm. The coated samples were heated to 600°C for 2 h in order to develop a good bond between the sample and platinum paste. Platinum wires were then connected to the samples. Impedance using the two probe method was measured in a frequency range typically from 0.1 Hz to 100 kHz with applied ac voltage amplitude of 0.01 V. A thermocouple was used to measure the sample temperature.

3. RESULT AND DISCUSSION

δ -Bi₂O₃ has a fluorite crystal structure which can be described as a face centered cubic packing of cations, with anions in all of the tetrahedral sites. It can also be described as simple cubic packing of anions with cations in the cubic (8-coordinate) sites. Therefore, these 25% oxygen vacancies are responsible for the ionic conduction of δ -Bi₂O₃. Due to the high ionic conductivity of the δ -Bi₂O₃ it is desirable to stabilize the cubic structure at room temperature. In this study the δ -Bi₂O₃ phase was stabilized at room temperature by the addition of Y₂O₃-Yb₂O₃ as co-dopants.

Figure 1 shows the X-ray diffraction patterns of samples having 12 and 18 mol% of co-dopant (Y₂O₃ and Yb₂O₃) sintered at 850°C for 24 h. It is seen that the cubic phase (δ -Bi₂O₃) is the sole crystalline phase which can be detected in all samples sintered at 850°C for 24 h. The X-ray diffraction patterns of samples containing 8 and 10 mol% co-dopant (Y₂O₃ and Yb₂O₃) sintered at 850°C for 24 h are shown in Figure 2.

Figure 2 shows that the tetragonal phase (β -Bi₂O₃) is the only crystalline phase in these experimental samples. This means that the Y₂O₃ and Yb₂O₃ as co-dopants could stabilize the cubic phase at room temperature in samples containing Bi₂O₃ up to 88 mol%. This could be compared with the Bi₂O₃ ceramics which

are stabilized by one dopant such as Y₂O₃. It has been reported that the cubic phase could be stabilized by 25 mol% dopant [1]. Therefore, using Y₂O₃ and Yb₂O₃ as co-dopant reduces the minimum amounts of dopant from 25 mol% to 12 mol%mol% for stabilizing the cubic bismuth oxide.

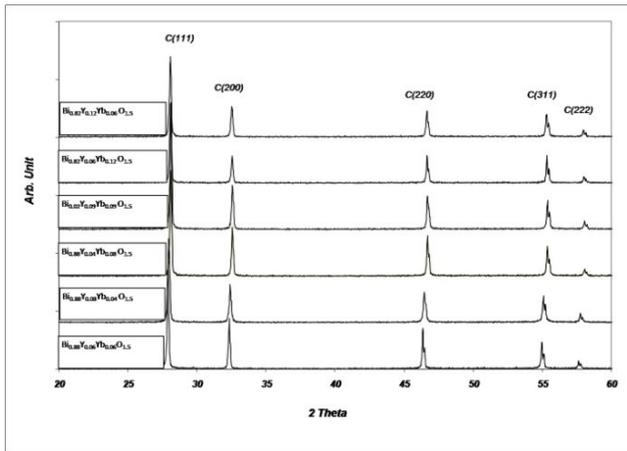


Figure 1. X-ray diffraction patterns of samples having 12 and 18 mol%mol% of co-dopant (Y_2O_3 and Yb_2O_3) that were sintered at $850^\circ C$ for 24 h

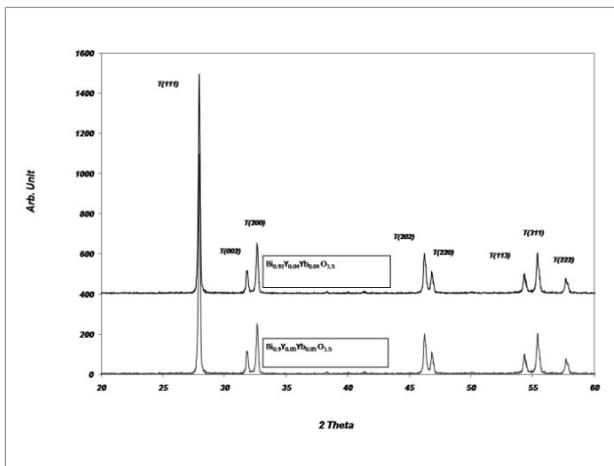


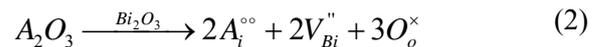
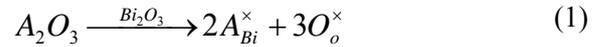
Figure 2. X-ray diffraction patterns of samples containing 8 and 10 mol%mol% co-dopant (Y_2O_3 and Yb_2O_3) that were sintered at $850^\circ C$ for 24 h

Due to the addition of dopants, a δ - Bi_2O_3 solid solution was created and shrinkage occurred in the δ - Bi_2O_3 structure. This phenomenon is the reason for the stabilization of δ - Bi_2O_3 structure at room temperature [12].

Ionic radii of Y^{3+} (1.02 Å) and Yb^{3+} (0.87 Å) are smaller than that of the Bi^{3+} ions. Therefore, Bi ions can be substituted by Yb and Y ions when these dopants are added to the Bismuth Oxide. As a result, the unit cell shrinks and the δ - Bi_2O_3 is stabilized due to this shrinkage.

Investigation on the substitution of Bi with the Yb and Y ions and production of solid solution was carried out by comparison of XRD patterns for

different samples, atomic distances and evaluation of the theoretical and experimental densities. The mechanism of this substitution is vacancies (V) or interstitials (i). According to Equations (1) and (2), Bi_2O_3 solid solution could be formed by substitution or as an interstitial solution of the Yb and Y ions solute atoms in the unit cell.



$$A = Y, Yb$$

where A_i : substituted ion, V_{Bi} : Bismuth Vacancy, (\times): null, ($\prime\prime$): Negative charge and ($\circ\circ$) positive charge.

Equation (1) suggests that in the Bi_2O_3 unit cell the Bi^{3+} cations could be replaced by Y^{3+} and Yb^{3+} , and oxygen ions are settled in the ionic positions of the lattice. But, Equation (2) suggests that instead, the Y^{3+} and Yb^{3+} may be dissolved in the unit cell as interstitial atoms, and oxygen ions could be settled in the ionic positions. In addition, Bi vacancies will be created for electrical balance, as the structure must be electrically neutral.

To assess the validity of these assumptions, the density was calculated by dividing the unit cell mass into the unit cell volume. Unit cell volume was calculated from the unit cell constant which in turn, was acquired by the least square method from XRD patterns of the sample. The unit cell mass was calculated according to Equations (1) and (2). Also, the experimental density was obtained by measuring the powder density using a helium gas pycnometer.

The calculated densities of $Bi_{0.88}Y_{0.04}Yb_{0.08}O_{1.5}$ sample, which contains the maximum amount of Yb_2O_3 are reported in Table 2.

TABLE 2. The calculated densities of $Bi_{0.88}Y_{0.04}Yb_{0.08}O_{1.5}$ sample, which contains the maximum amount of Yb_2O_3

Equation	Calculated Density (g/cm^3)
1	8.9101
2	5.2676

Comparing the data reported in Table 2 with the experimentally measured density of $8.9210 (g/cm^3)$

of the sample shows that the substitution of Bi cations by dopants cations in a fluorite structure according to Equation (1) is acceptable. This hypothesis has also been confirmed by others [13].

Y^{3+} and Yb^{3+} cations have smaller ionic radii than the Bi^{3+} ; therefore, substitution of Bi by these co-dopants causes shrinkage of the unit cell.

For the other samples: ($Bi_{0.88}Y_{0.06}Yb_{0.06}O_{1.5}$, $Bi_{0.88}Y_{0.08}Yb_{0.04}O_{1.5}$ and $Bi_{0.88}Y_{0.04}Yb_{0.08}O_{1.5}$), the shrinkage of unit cell was investigated by measuring the lattice constant using the least square method (Table 3).

Table 3 shows that the lattice constant of components having the mixture of Y_2O_3 and Yb_2O_3 as co-dopants are smaller than that of the pure bismuth oxide. This means that the δ - Bi_2O_3 solid solution with cubic structure has been stabilized at room temperature because of the unit cell shrinkage. This observation is in agreement with other investigations [12].

TABLE 3. Lattice constant of components having the mixture of Y_2O_3 and Yb_2O_3 as co-dopants and pure bismuth oxide

Sample	Lattice parameter(Å)
$Bi_2O_3 \delta$	5.6480
$Bi_{0.88}Y_{0.06}Yb_{0.06}O_{1.5}$	5.5440
$Bi_{0.88}Y_{0.08}Yb_{0.04}O_{1.5}$	5.5507
$Bi_{0.88}Y_{0.04}Yb_{0.08}O_{1.5}$	5.5202

Solid electrolytes have to work at a high temperature for a long time; therefore, their properties should be stable at the working temperature during their service life. For that reason the effect of aging time on crystalline phase stability of $Bi_{0.88}Y_{0.06}Yb_{0.06}O_{1.5}$, $Bi_{0.88}Y_{0.08}Yb_{0.04}O_{1.5}$ and $Bi_{0.88}Y_{0.04}Yb_{0.08}O_{1.5}$ samples was investigated at $600^\circ C$ for 72–352h. (Figures 3, 4 and 5).

Figure 3 shows that δ - Bi_2O_3 is the sole crystalline phase in the sample that contained 6 mol% Y_2O_3 and 6 mol% Yb_2O_3 as co-dopants ($Bi_{0.88}Y_{0.06}Yb_{0.06}O_{1.5}$) after aging at $600^\circ C$ for 72h. But, after 120h the sample undergoes a transformation to β - Bi_2O_3 with tetragonal structure. By further increasing the aging time to 352h, the tetragonal phase is the only crystalline phase which is detected in the XRD patterns of sample $Bi_{0.88}Y_{0.06}Yb_{0.06}O_{1.5}$.

β - Bi_2O_3 type crystal structure is a two-dimensional super-structure of δ - Bi_2O_3 [2]. This means that with a short replacing distance of cations in δ - Bi_2O_3 lattice, the tetragonal phase will be formed. Formation of the tetragonal solid solution is a very slow process requiring a long heat treatment [2]. It has been reported that when cations with small cationic radii such as Yb^{3+} are introduced to bismuth oxide, a tetragonal phase will be formed[6]; however, the reason for this process is not clear yet.

Figure 4 shows the phase transition of samples containing 8 mol%mol% Y_2O_3 and 4 mol%mol% Yb_2O_3 as co-dopants ($Bi_{0.88}Y_{0.08}Yb_{0.04}O_{1.5}$) after aging at $600^\circ C$ for 72-352 h. It is seen that the tetragonal phase has formed after aging for 72 h at $600^\circ C$ and it has not changed up to 352 h of aging.

Comparing the results of Figures. 3 and 4 reveals that the phase transition rate in the $Bi_{0.88}Y_{0.08}Yb_{0.04}O_{1.5}$ is faster than that in the $Bi_{0.88}Y_{0.06}Yb_{0.06}O_{1.5}$ sample. That is, the cation movement in the $Bi_{0.88}Y_{0.08}Yb_{0.04}O_{1.5}$ lattice is faster than that in the $Bi_{0.88}Y_{0.06}Yb_{0.06}O_{1.5}$ lattice. It can be seen from Table 3 that the lattice parameter of the $Bi_{0.88}Y_{0.08}Yb_{0.04}O_{1.5}$ is larger than that of $Bi_{0.88}Y_{0.06}Yb_{0.06}O_{1.5}$; therefore, the movement of cations in $Bi_{0.88}Y_{0.08}Yb_{0.04}O_{1.5}$ is easier than that in the $Bi_{0.88}Y_{0.06}Yb_{0.06}O_{1.5}$. As a result, the cubic phase transformation to tetragonal in $Bi_{0.88}Y_{0.08}Yb_{0.04}O_{1.5}$ is faster than that in the $Bi_{0.88}Y_{0.06}Yb_{0.06}O_{1.5}$ samples.

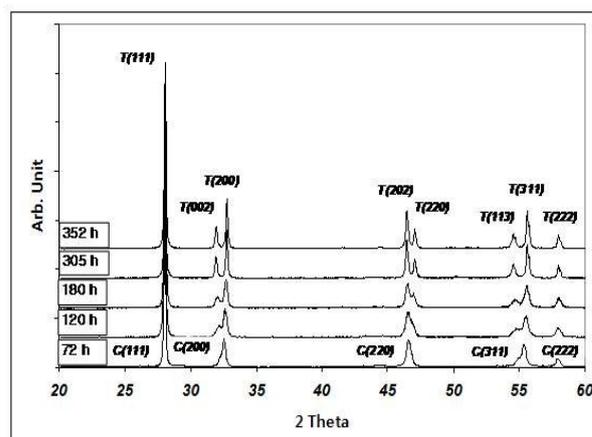


Figure 3. X-ray diffraction patterns of $Bi_{0.88}Y_{0.06}Yb_{0.06}O_{1.5}$ that aged at $600^\circ C$ for durations of 72 – 352 h

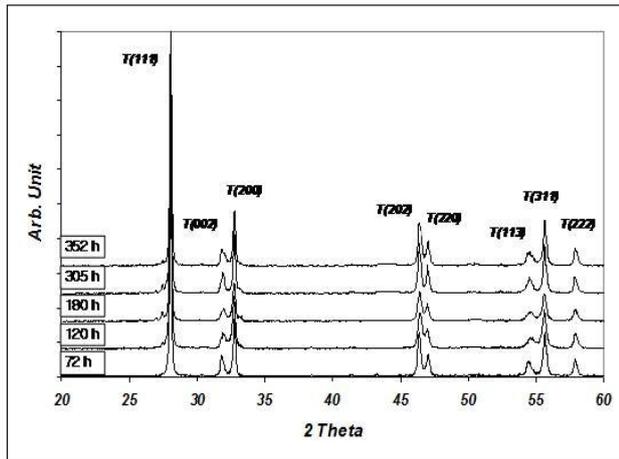


Figure 4. X-ray diffraction patterns of $\text{Bi}_{0.88}\text{Y}_{0.08}\text{Yb}_{0.04}\text{O}_{1.5}$ that aged at 600°C for durations of 72 – 352 h

Figure 5 shows the phase transition in the sample containing 4 mol%mol% Y_2O_3 and 8 mol%mol% Yb_2O_3 as co-dopants ($\text{Bi}_{0.88}\text{Y}_{0.04}\text{Yb}_{0.08}\text{O}_{1.5}$) after aging at 600°C for 72-352h. It can be seen that, the cubic phase is stable up to 120h of aging at 600°C . Subsequent phase transformation takes place after 180h of aging that forms the tetragonal phase. Table 3 shows that the lattice parameter of $\text{Bi}_{0.88}\text{Y}_{0.04}\text{Yb}_{0.08}\text{O}_{1.5}$ is smaller than the other samples; therefore, it is more stable during the aging period.

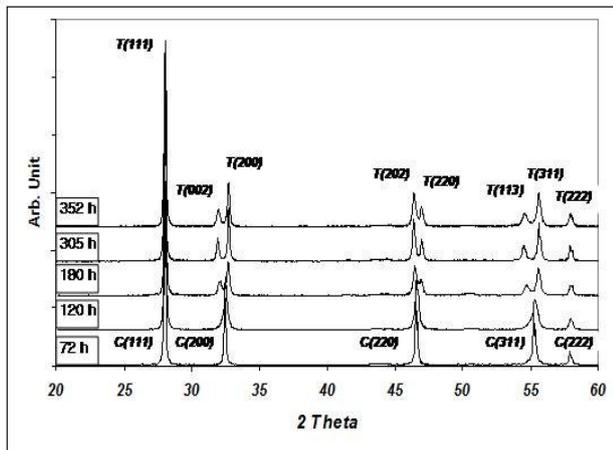
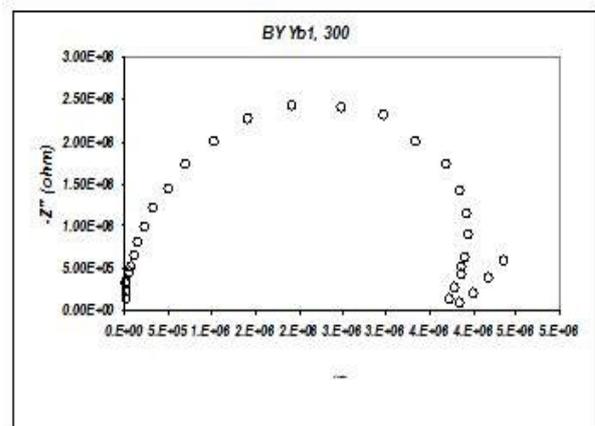


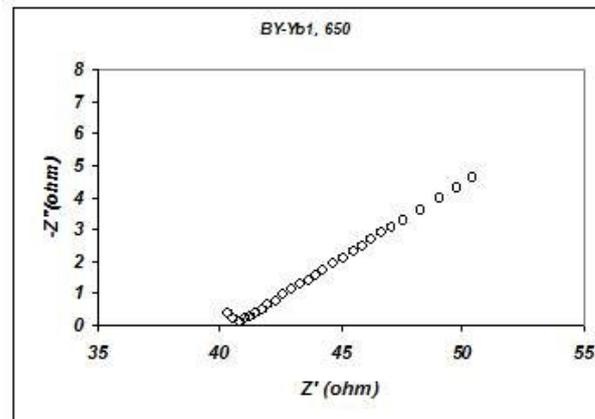
Figure 5. X-ray diffraction patterns of $\text{Bi}_{0.88}\text{Y}_{0.04}\text{Yb}_{0.08}\text{O}_{1.5}$ that aged at 600°C for durations of 72 – 352 h.

Figure 6 shows the impedance spectra for $\text{Bi}_{0.88}\text{Y}_{0.08}\text{Yb}_{0.04}\text{O}_{1.5}$ at (a) 300°C and (b) 650°C . The conductivities were calculated from the values

of the bulk resistance measured at the frequency corresponding to the appropriate minima in the complex plots. Figure 6-a shows that at 300°C , the plot of imaginary versus real components of impedance forms a semicircle at high frequency which is attributable to the bulk resistance. As the temperature increase to 650°C , in the low frequency end of the spectrum another semicircle appears. The high frequency end of the low frequency semicircle is linear and intercepts the real axis at 45° . This semicircle has been attributed to the electrode interfacial resistance and is described as a Warberg-type impedance indicating gas diffusion at the electrode [14].



a



b

Figure 6. the impedance spectra for $\text{Bi}_{0.88}\text{Y}_{0.08}\text{Yb}_{0.04}\text{O}_{1.5}$ at (a) 300°C and (b) 650°C

The logarithm of the bulk conductivity was plotted as a function of reciprocal temperature for different samples in Fig. 7. $\text{Bi}_{0.88}\text{Y}_{0.08}\text{Yb}_{0.04}\text{O}_{1.5}$ sample showed higher conductivity than the

$\text{Bi}_{0.88}\text{Y}_{0.06}\text{Yb}_{0.06}\text{O}_{1.5}$ and $\text{Bi}_{0.88}\text{Y}_{0.04}\text{Yb}_{0.08}\text{O}_{1.5}$ samples. From Fig. 7, it is also clear that the conductivity of these samples is higher than those of BY25 (75mol%mol% Bi_2O_3 -25mol%mol% Y_2O_3).

A change in the activation energy of the samples was observed, with decreasing activation energy above 600°C and increases in activation energy below 600°C.

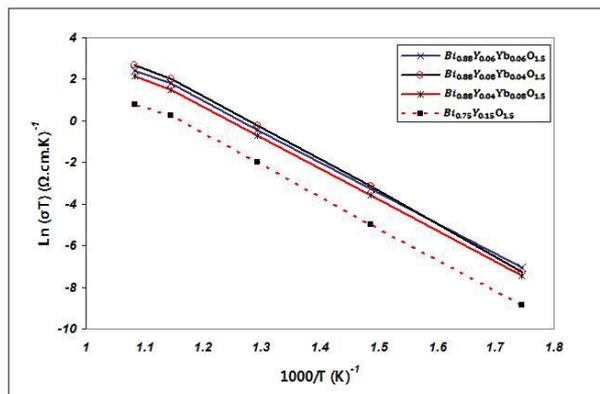


Figure 7. Logarithm of the bulk conductivity for different samples

This change in activation energy may be attributed to an order–disorder transition of the oxygen sublattice [6, 13].

4. CONCLUSION

In this study we have stabilized the δ - Bi_2O_3 phase at room temperature by making a mixture of Bi_2O_3 doped with Y_2O_3 and Yb_2O_3 , and then investigated the stability of the δ phase at different aging times. The samples were prepared by isostatic pressing and sintering at 850°C. The performed X-ray diffraction analysis detected cubic phase (δ - Bi_2O_3) as the sole stable crystalline phase in the samples having 12 and 18 mol%mol% of Y_2O_3 and Yb_2O_3 . The tetragonal phase was also observed in samples with 8 and 10% mol additives.

The presented results reveal that:

- Aging of samples shows that a phase transformation occurs in doped samples.
- Samples with a mixture of two additives (Bi_2O_3 with Y_2O_3 and Yb_2O_3) have higher conductivity than samples with one additive (Bi_2O_3 with Y_2O_3).

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