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Synthesis of bismuth doped yttria stabilized zirconia electrolyte and study of ionic conductivity

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ABSTRACT

$x\%$ mol Bi^{3+} -doped yttria-stabilized zirconia with 4% mol $\text{YO}_{1.5}$ ($x=0-5$, BiYSZ) are prepared via lamellar liquid crystal template method. The influence of different doping amount of Bi^{3+} on crystal form, morphology, the ionic conductivity are investigated in detail. In addition, densification time of BiYSZ are determined. X-ray diffraction (XRD), Raman spectrum, Scanning Electron Microscope (SEM) results show that BiYSZ powder with stable tetragonal phase and spherical structure is nanometer level. Moreover, by using the AC impedance spectroscopy to analyse conductivity of solid electrolytes, we find that Bi^{3+} -doped yttria-stabilized zirconia with 4% mol $\text{YO}_{1.5}$ improve the ionic conductivity. Comparing all the compositions, 3 mol% Bi^{3+} doped yttria stabilized zirconia with 4% mol Y^{3+} gives the highest ionic conductivity of $7.41 \times 10^{-5} \text{ S/cm}^{-1}$ at 500°C , and sintering temperatures of BiYSZ reduce around 100°C than $\text{Y}_{0.04}\text{Zr}_{0.96}\text{O}_2$ (4YSZ), ionic conductivity increases one order of magnitude.

Keywords: BiYSZ; Doped; Crystal; Ionic conductivity

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1、 introduction

Solid oxide fuel cells (SOFCs) have attracted attention as an ecofriendly and highly efficient power generation system^[1]. Electrolyte is the core component of SOFC. The typical oxygen ion solid electrolyte has ZrO₂-based, CeO₂-based, Bi₂O₃-based, ABO₃ perovskite type and so on. Yttria-stabilized zirconia (YSZ) is generally used as a solid electrolyte because of its high oxygen ion conductivity and chemical stability at high temperatures(over 800 °C)^[2, 3]. However, ionic conductivity and sintering temperature of the sample need to be improved in order to popularization and application of solid oxide fuel cell at intermediate temperatures(400-650°C, IT-SOFC)^[2, 4].

Powder preparation, solid forming and high temperature sintering are three important stages of electrolyte preparation process. Therefore, there are many factors affecting the ionic conductivity. Recent reports have suggested that co-doping strategy is an effective method for improving electrical conductivity of solid electrolytes^[5, 6]. At present, most studies have doped commercial yttria-stabilized zirconia to change its electrical properties by regulating the crystal phase, morphology and particle size distribution. In addition, many groups have prepared different levels powder by different techniques to further decrease the ohmic resistance of solid electrolyte, for example, chemical coprecipitation method^[7], sol-gel methods^[8] and so on. Rudzani

sigwadi^[9] prepared zirconia with relatively small particle size and small distance between lattice fringes (0.2928 nm and 0.2824 nm) by precipitation method, and the effect of calcination temperature on the crystallinity and particle size of zirconia particles was investigated. In this paper, lamellar liquid crystal template method is first adopted, which has the important advantage of mild reaction conditions, and enables synthesis of nanopowder at low temperature.

Bismuth oxides stabilized with lanthanide dopants in a fluorite structure (δ -Bi₂O₃) are known for superior ionic conductivity^[10, 11], but they reduce to metallic Bi under reducing atmosphere and undergo a transformation to a low ionic conductive phase at the operation temperatures^[12, 13]. So bismuth oxides cannot be utilized as stand-alone electrolytes^[14]. Gil and others have proved the addition of Bi₂O₃ can reduce the sintering temperature of gadolinium-doped ceria (GDC) electrolytes by about 250-300°C^[15]. In another report, densification of the GDC electrolyte was achieved at a low sintering temperature of 1000-1200°C by adding Bi₂O₃ as dopant^[16, 17]. Hirano^[18] reported that doping with 1 mol% Bi₂O₃ decreased the sintering temperature of scandia-stabilized zirconia ceramics by 300°C, while allowing its electrical conductivity at 1000°C and 800°C to reach 0.33 and 0.12 S/cm, respectively. As a sintering aid, Bi₂O₃ is also a very good oxygen ion conductor. Therefore, adding Bi³⁺ to zirconia oxide may not only improve ionic conductivity, but also decrease sintering temperature.

Based on the above analysis, bismuth oxide doped yttrium oxide stabilized zirconia are synthesized by lamellar liquid crystal template method in this

work.,which aims to regulate the powder structure by template with SDS/C₁₀H₂₂O/H₂O,further improve its electrical conductivity by doping ZrO₂-based solid electrolyte.

2 Experimental

2.1 Synthesis of powder and electrolyte

As raw materials with Bi(NO₃)₃•5H₂O,(Y(NO₃)₃•6H₂O,C₁₀H₂₂O,H₂O, ZrOCl₂•8H₂O,C₁₂H₂₅NaSO₄(SDS),composite powder of Y_xZr_{1-x}O₂ and Bi_xY_{0.04}Zr_{0.96-x}O₂ are prepared via lamellar liquid crystal template method. Bi(NO₃)₃•5H₂O,(Y(NO₃)₃•6H₂O,C₁₀H₂₂O,ZrOCl₂•8H₂O are purchased from Aladdin Biochemical Technology Co.,Ltd.The manufacturer of C₁₂H₂₅NaSO₄(SDS) and NH₃•H₂O(25%-28%) are Tianjin Yong sheng Fine Chemical Co.,Ltd. H₂O is from Inner Mongolia University of Technology.

First,lamellar liquid crystal template is made of SDS,C₁₀H₂₂O and H₂O prepared at mass ratio of 15:10:75.The stock solution is prepared by dissolving stoichiometric Bi(NO₃)₃•5H₂O in nitric acid,and (Y(NO₃)₃•6H₂O and ZrOCl₂•8H₂O in water,making concentration of Zr⁴⁺ is 1mol/L in the total solution.Then pouring into the SDS/C₁₀H₂₂O/H₂O ternary system.The resulting solution stand 12h at 25°C in thermostat waterbath.Precipitation is carried out by adding 5mol/L NH₃•H₂O to the solution after 12h.The pH value is controlled in 8–9 at the end.Then,mix solution in centrifuge after 12h at 9000 r/min speed with alcohol and water alternately clean 7min, until foam is eliminated.Next,the precursor of Bi³⁺-doped yttria stabilized zirconia

was dried in a vacuum drying oven at 80 °C for 12h. Finally, the dried sample undergoes calcination (700°C, 2h), pressing, gluing, sintering and silver-coating to synthesize solid electrolytes. $Y_xZr_{1-x}O_2$ and xBi^{3+} doped yttria-stabilized zirconia with 4% mol Y^{3+} ($x=1-5\%$ mol) ceramic disks are sintered in air atmosphere for 2h at 1200°C and 1100°C respectively. In addition, diameter and thickness of ceramic disks are 12mm and 1mm, respectively.

2.2. Characterization of powder and electrolyte

X-ray powder diffraction (XRD) analysis mainly analyzes the phase structures, crystal form and cell parameters of the samples. The data are collected using the Rigaku SmartLab-9kW (Japan). Test conditions are as follows: Cu K α radiation, $2\theta = 20-80$. XRD can calculate grain size by Scherrer formula,

$$D = K\lambda / B \cos\theta \quad (1)$$

Where D is grain size, B is Half-peak width of diffraction peak, θ is Bragg diffraction angle, K and λ is a constant of 0.89 and 0.154056 respectively.

Phase structures are further confirmed via using InVia Microscope Raman. The relative density of the sintered disk is determined via Archimedes' method using GP-120C Precision Ceramic Porosity Volume Density Test. Morphology of powders are observed by scanning electron microscope (SEM) with Hitachi, Su8220 (Japan).

The electrical properties of the samples are measured using the AC impedance spectroscopy, which adopts a high temperature dielectric temperature spectrometer HDMS-1000 of Wuhan Bailibo Technology Co., Ltd. Test conditions are as follows: $T=300^\circ\text{C}-500^\circ\text{C}$, 50°C intervals, the frequency range is 20 Hz-1MHz. The

impedance data is gained from intersection of AC impedance spectroscopy with x-axis, the conductivity is calculated from following equation^[19]:

$$\sigma = L/AR \quad (2)$$

Where L is the disk thickness.A is its superficial area,R is the resistance calculated from the impedance spectra.The activation energy (E_a) of the conductivity is determined by the Arrhenius law:

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad (3)$$

Where σ_0 is the pre-exponential factor,T is testing temperature(K),k is the Boltzmann constant, E_a is activation energy.

3、 Results and discussions

3.1. Phase structure characterization

Fig.1 shows the XRD and Raman patterns of different amount(0-5%mol) of Bi³⁺-doped yttria stabilized zirconia nanopowders calcined at 973 K for 2h under air atmosphere.All diffraction peaks of these patterns match with cubic and tetragonal structure l(PDF#50-1089).Because the diffraction peaks of tetragonal and cubic phases have similar diffraction patterns,it is difficult to distinguish the cubic phase or the tetragonal phase accurately by XRD.However,Raman spectra can further determine crystal phase of the sample.As can be seen from the diagram,the diffraction peaks of synthesized powder correspond to the tetragonal phase^[20].The XRD and Raman results show that the phase structures of the sample is tetragonal phase, in other words, the addition of Bi (NO₃)₃ also stabilizes zirconia in the tetragonal phase.

Fig1

Fig.2 investigates the XRD diffraction pattern of 3%mol Bi³⁺-doped 4YSZ (3Bi4YSZ) samples sintered at varying temperatures. Diffraction shows that the sample are monocline phase at 1050°C and 1150°C, however, still is tetragonal phase at 1100°C. Which may be it makes that yttrium distributes to the lattice gap, further forms lattice association to changing of sintering temperature in fixed doping amount of bismuth nitrate.

Fig.2

3.2 XPS analysis

XPS surveys of ZrO₂, 4YSZ, 3Bi4YSZ samples are shown in Fig.3. The presence of Y3p, Y3d, Bi4d in 4YSZ and 3Bi4YSZ compared with ZrO₂, which further indicate that Y, Bi have been incorporated into the zirconia lattice. In addition, Table 1 varies in lattice constant of BiYSZ, which represents the dopant enters the lattice of zirconia.

Fig.3

Table 1

3.3 Microstructure analysis

Scanning electron microscope images of BiYSZ nanopowders in 200k multiple are shown in Fig.4 a-f, which show the addition of Bi(NO₃)₃ don't affect the morphology, size and dispersion of the samples. With the increase of the content of bismuth nitrate, BiYSZ powder is still monodisperse spherical structure with a diameter less than 15nm. Table 2 shows particle size of BiYSZ obtained by different methods. A is

calculated by Scherrer formula, B is gained by Jade6 software. The average particle sizes both tend to decrease first and then increase, and the total particle size are controlled within 15nm.

Fig.4

Table2

Fig.5 gives SEM images of 4YSZ(a=1200 °C) and 3Bi4YSZ(b=1100 °C) after sintering. As can be seen from Fig.6(a), density of 4YSZ sample is still lacking. On the one hand, the equipment may limit the increase of temperature, on the other hand, multiple of the scanning equipment also may limit its clarity. While the sintering density decreases, and the grain and grain boundary melts, which leads to the spherical shape of the grain in Fig.6(b). The resulting densities both are shown in Table 3.

Fig.5

3.4 Electrical conductivity

The corresponding equivalent circuit is shown in Fig.6. The typical AC impedance spectra of ionic conductor consist of two semicircles and a diagonal line. High and low frequency semicircles correspond to grain impedance and grain boundary impedance respectively, and diagonal lines correspond to resistance and capacitance effect of electrode. Grain and grain boundary impedance of the sample can be obtained by the intersection of semicircle and spectrum x axis.

At the same time, Fig.6 gives the AC impedance spectra or Nyquist plot of BiYSZ at 500 °C. 3Bi4YSZ is shown in the insert of Fig.6. The lines in Fig.6 are the experiment data and the different symbols with different colors are the fitting results. Due to the

relaxation properties of different materials and the relatively high measurement temperature, the high-frequency semicircle of 4YSZ sample represents its grain boundary resistance, and the grain resistance is calculated via the horizontal intercept of the high frequency curve^[21]. In the 4YSZ sample, the total resistance mainly comes from the grain resistance. While in BiYSZ sample, with the increase of doping amount, the grain boundary semicircle become gradually intact, and the electrode line begins to appear, until the doping amount increases to 4mol%, the electrode line disappears. On the whole, grain resistance, grain boundary resistance and total resistance decrease rapidly first, then increase rapidly, finally decrease rapidly, and resistance is minimized at $x=0.03$, that is $R_g=950\Omega$, $R_g+R_{gb}=1420\Omega$. Comparing show that the doping amount is 3mol% is better, and the conductivity is 7.41×10^{-5} by formula (2).

Fig.6

Fig.7 shows Arrhenius plots for the total ion conductivity of BiYSZ. The total ion conductivity varies in a straight line with the change of temperature in the detection temperature range (300-500°C). The sample activation energy is calculated by slope and formula (3), minimum activation energy is 0.72eV ($x=0.03$). Grain conductivity, grain boundary conductivity, total ionic conductivity, sintering temperature and activation energy of 4YSZ and 3Bi4YSZ are listed in Table 3. The reason for the result may be the melting point of Bi_2O_3 is lower than ZrO_2 , while melting point of ZrO_2 is, so the sintering temperature is too high to cause the phenomenon of over-sintering, the grain boundary is spherical, and then the density is

reduced^[22]. However, due to the good conductivity of bismuth nitrate itself, its conductivity has increased. In 3Bi4YSZ sample exhibits the highest conductivity of 7.41×10^{-5} S/cm at 500°C, while the conductivity of 4YSZ sintered at 1200°C is about 3.26×10^{-6} S/cm at 500 °C, demonstrating that adding Bi(NO₃)₃ improves the conductivity to about one order of magnitude, and decreases of 100°C in sintering temperature.

Fig.7

Table3

Fig.8 studies the effects of the sintering condition, found that 3Bi4YSZ sintered at 1100°C for 2.5h and 3h had a lower conductivity compared with 2h. Therefore, sintering time of 2h was determined.

Fig.8

4、 conclusions

Spherical BiYSZ with tetragonal structure nano-powders are prepared via lamellar liquid crystal template method. Tetragonal ZrO₂ can be obtained via doping 4mol % of Y(NO₃)₃ and 0-5mol% of Bi(NO₃)₃ into its lattice. The addition of Bi(NO₃)₃ and the nanocrystallization of the powder BiYSZ increase the ionic conductivity of the electrolyte. It is confirmed that 3mol% Bi(NO₃)₃ doped yttria stabilized zirconia raise in ionic conductivity at 500°C and reduce sintering temperature.

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Xia Guo:Data curation, Writing-original draft preparation. **Xiaobing Zhao:** Validation, Supervision. **Weiyan He:** Reviewing , Revising.

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Captions

Fig.1 XRD and Raman patterns of BiYSZ nanopowders calcined at 973 K for 2h under air atmosphere.

Fig.2 XRD patterns of 3mol%Bi³⁺ doped 4YSZ nanopowders sintered at 1050°C、1100°C、1150°C

Fig.3 XPS survey of ZrO₂、4YSZ and 3Bi4YSZ

Fig.4 SEM images of xBi³⁺ doped yttria stabilized zirconia with 4mol%Y³⁺

Fig.5 SEM images of 4YSZ(a=1200°C)and 3Bi4YSZ(b=1100°C) after sintering

Fig.6 Equivalent circuit diagram and the Ac impedance spectra measured at 500°C in air atmosphere for BiYSZsintered at 1100°C(note:sintering temperature of x=0 is1200°C)

Fig.7 Arrhenius plots for the total ion conductivity of Bi_xY_{0.04}Zr_{0.96-x}O₂ with x=0.00-0.05

Fig.8The impedance spectra of Bi_{0.03}Y_{0.04}Zr_{0.93} in sinter time with 2h、2.5h、3h

Table1 The lattice constant of BiYSZ

Table2 Particle size of BiYSZ obtained by different methods

Table3 grain and grain boundary conductivity, total ionic conductivity,sintering density and activation energyof $Y_{0.04}Zr_{0.93}O_2$ and $Bi_{0.03}Y_{0.04}Zr_{0.93}O_2$

Table1 The lattice constant of BiYSZ

Sample	a=b(nm)	c(nm)	烧结温度(°C)
4YSZ	0.3608	0.5160	1200
1BiYSZ	0.3591	0.5222	1100
2BiYSZ	0.3591	0.5256	1100
3BiYSZ	0.3612	0.5192	1100
4BiYSZ	0.3603	0.5164	1100
5BiYSZ	0.3612	0.5262	1100

Table2 Particle size of BiYSZ obtained by different methods

Sample	A(nm)	B(nm)
$Y_{0.04}Zr_{0.96}O_2$	12.86	10.4
$Bi_{0.01}Y_{0.04}Zr_{0.95}O_2$	11.94	8.9
$Bi_{0.02}Y_{0.04}Zr_{0.94}O_2$	10.45	8
$Bi_{0.03}Y_{0.04}Zr_{0.93}O_2$	10.44	9.5
$Bi_{0.04}Y_{0.04}Zr_{0.92}O_2$	12.45	10.3
$Bi_{0.05}Y_{0.04}Zr_{0.91}O_2$	13.96	11.6

Table3 grain and grain boundary conductivity, total ionic conductivity, sintering

density and activation energy of $Y_{0.04}Zr_{0.93}O_2$ and $Bi_{0.03}Y_{0.04}Zr_{0.93}O_2$

Sample	Grain conductivity	Grain boundary conductivity	Total(S/cm) conductivity	Activation (ev)	Sintering density(%)
4YSZ	3.26×10^{-6}	--	3.26×10^{-6}	0.85	96
3BiYSZ	1.11×10^{-4}	2.24×10^{-4}	7.41×10^{-5}	0.72	65

Figures

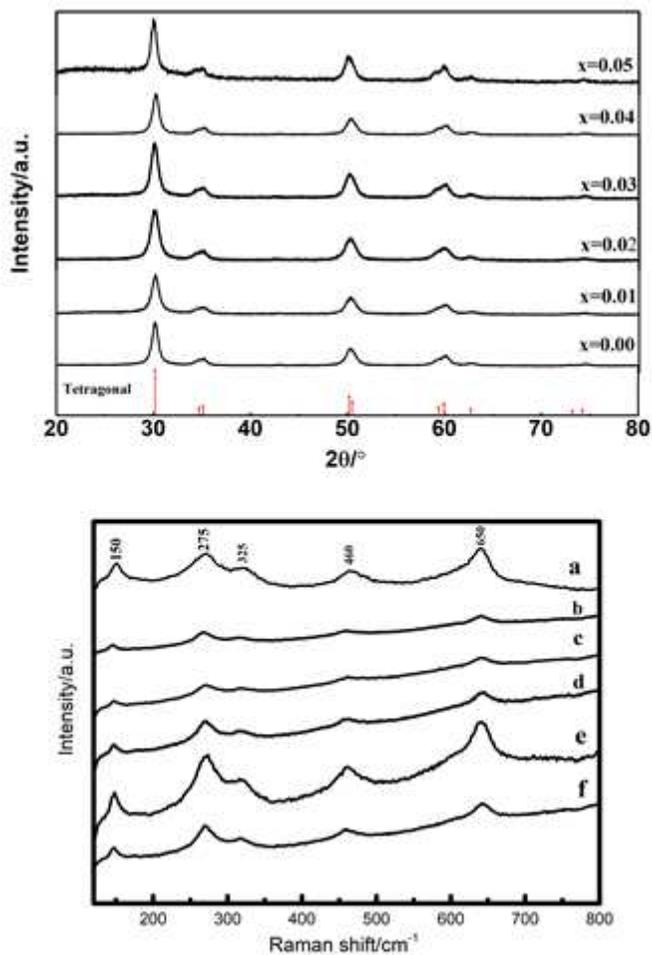


Figure 1

XRD and Raman patterns of BiYSZ nanopowders calcined at 973 K for 2h under air atmosphere.

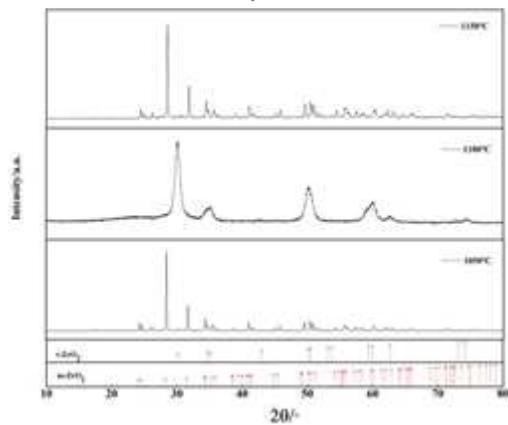


Figure 2

XRD patterns of 3mol%Bi³⁺ doped 4YSZ nanopowders sintered at 1050 °C, 1100 °C, 1150 °C

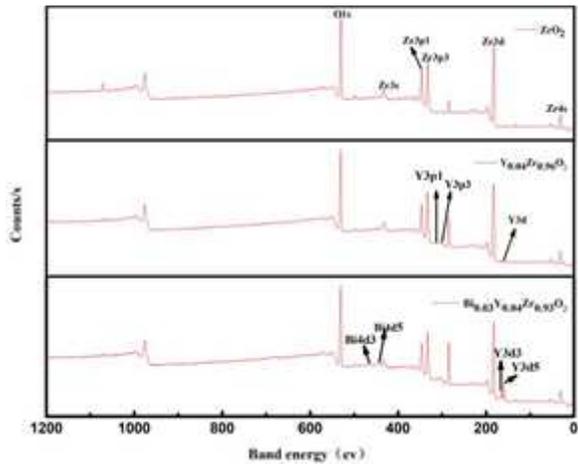


Figure 3

XPS survey of ZrO_2-4YSZ and $3Bi4YSZ$

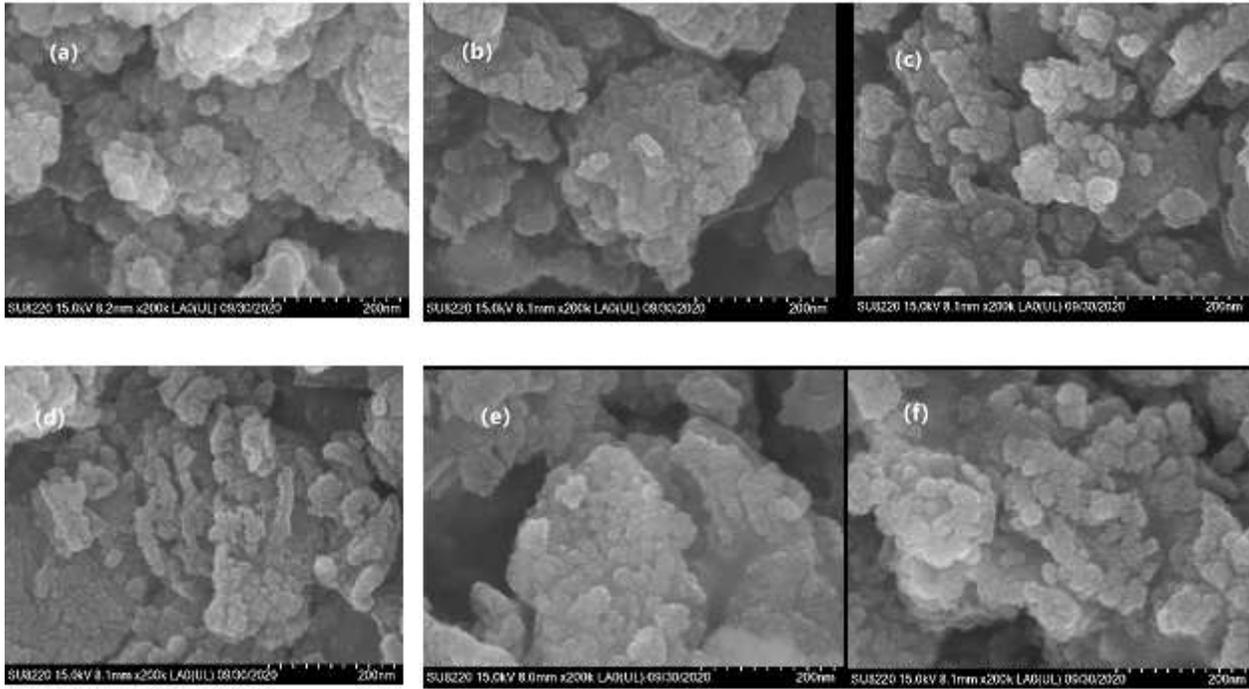


Figure 4

SEM images of xBi^{3+} doped yttria stabilized zirconia with 4mol% Y^{3+}

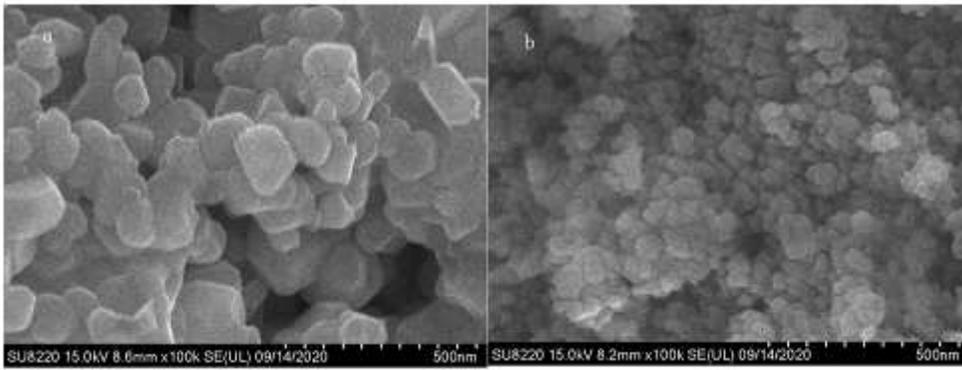


Figure 5

SEM images of 4YSZ(a=1200 \AA) and 3Bi4YSZ(b=1100 \AA) after sintering

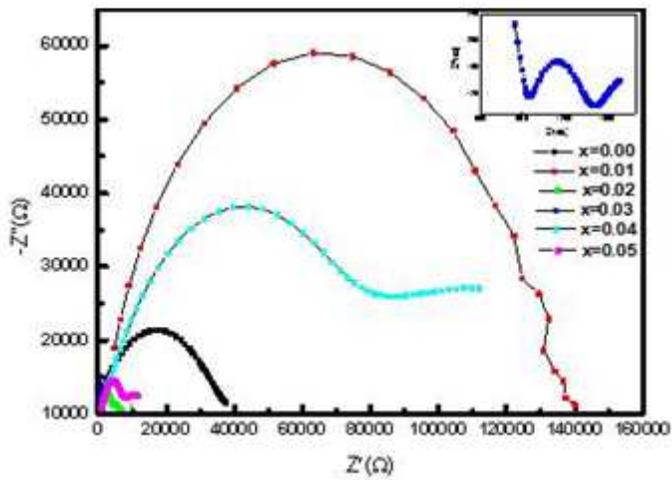
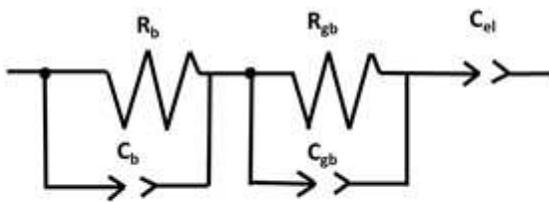


Figure 6

Equivalent circuit diagram and the Ac impedance spectra measured at 500 \AA in air atmosphere for BiYSZ sintered at 1100 \AA (note:sintering temperature of x=0 is1200 \AA)

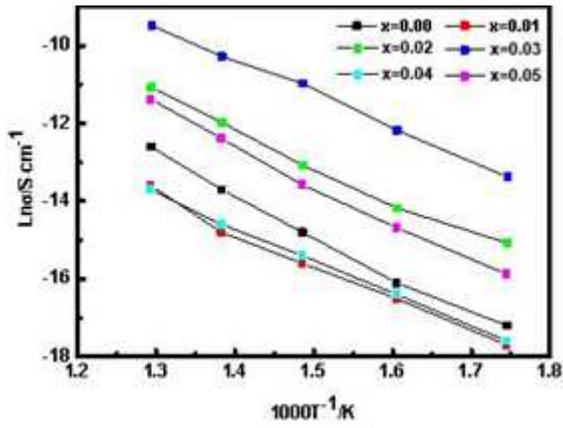


Figure 7

Arrhenius plots for the total ion conductivity of $\text{Bi}_x\text{Y}_{0.04}\text{Zr}_{0.96-x}\text{O}_2$ with $x=0.00-0.05$

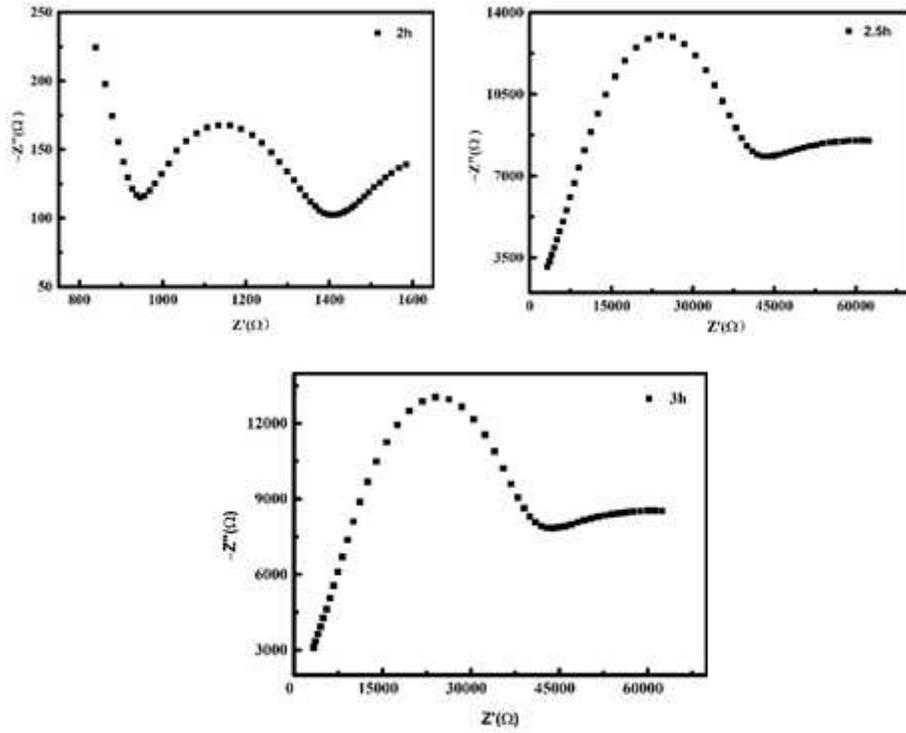


Figure 8

The impedance spectra of $\text{Bi}_{0.03}\text{Y}_{0.04}\text{Zr}_{0.93}$ in sinter time with 2h, 2.5h, 3h