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Effect of microwave sintering on properties of Erbia stabilized bismuth oxide prepared by auto combustion method for IT- SOFC electrolytes

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Abstract: Bismuth oxide based ceramics show the highest oxide ion conductivity even below 500 ^{0}C, they are expected to be promising material for solid electrolyte of IT-SOFC. Pure bismuth oxide however transforms to monoclinic phase on cooling below 730 ^{0}C. The cubic phase at high temperature can be stabilized down to room temperature by the additions of Erbia. In this work 20 mole% Erbia stabilized bismuth oxide ($Bi_{0.8}Er_{0.2}O_{1.5}$) nano powder has been prepared by Citrate–Nitrate auto combustion method. Thermal analysis of as-synthesized powder is done by DTA /TGA. Powder is calcined at 700 ^{0}C for 4 hours and X-Ray diffraction pattern confirm the cubic phase bismuth oxide (JCPDS file 20-0052). Powder is compacted into pellets under 5 ton load and sintered using microwave furnace at 900 ^{0}C for 15 min. Density of more than 97% of theoretical value has been found. Impedance analysis shows higher ionic conductivity 0.035 S/cm at 500^{0}C which is 1.5 times more compared to conventional sintered samples sintered at 1000 ^{0}C. SEM analysis confirms uniform grain size with almost negligible porosity.
Keywords: IT-SOFC, Erbia stabilized Bismuth Oxide, Auto Combustion, and Microwave Sintering.

1. Introduction and Experimental :

The advantages of lowering the operation temperature of SOFCs have attracted great interest worldwide. Decreased operation temperature however requires increased electrolyte ionic conductivity and enhanced electrode reaction activity [1]. Bismuth oxide based electrolytes was found to be excellent electrolytes with high ionic conductivity at lower temperature. The highest ionic conductivity was found in ESB (20 mol% Er_2O_3 stabilized Bi_2O_3) solid solution having fluorite structure [2-4]. The application of microwave sintering in processing various kinds of ceramic materials in an efficient, economic and emerging as an innovative technology with great commercial potential and many attractive advantages. In this process there is no thermal conductivity mechanism involved, the heating is instantaneous and rapid, and is a function of the material under process. The heat is generated internally within the material instead of originating from the external sources[5] .In this present work in order to increase the conductivity at lower temperature of ESB by taking citrate-nitrate auto-combustion route for powder preparation and did microwave sintering and then did the characterization to see the effect on properties of ESB.

Powders of $Bi_{0.8}Er_{0.2}O_{1.5}$ (ESB) were synthesized by citrate-nitrate auto-combustion technique [6]. Erbium oxide was converted into its nitrate solution by dissolving it in nitric acid. Aqueous solutions of Bismuth nitrate, and citric acid were prepared separately and mixed in appropriate amounts maintaining the citrate to nitrate (C/N) ratio as 0.3 to have a controlled combustion [7]. The mixed solution was evaporated by heating on a hot plate using a magnetic stirrer at ~ 200 ^{0}C till it became gel. The gel slowly foamed and finally gets ignited on its own to produce dark yellow powder. The whole process after completion gives rise to yellow colour powder (ash).DSC analysis of green ash done by NETZSCH DSC 404F3 upto 900 ^{0}C. The powder (ash) was calcined at 700°C for 4 h. The calcined powder was pelletized under a load of 60kN into cylindrical pellets. The pellets were sintered at 900 ^{0}C for 30 minute at the rate of 25 ^{0}C /minute using microwave sintering furnace (Enerzi Microwave systems). Powder X-ray diffraction (XRD) patterns of calcined powder and sintered pellets were recorded using Rigaku X-ray diffractometer employing Cu Kα radation with Ni filter for determination of crystal structure and phases present. Experimental density was determined using Archimedes principle. Microstructural studies of polished and thermally etched sintered pellets done by taking micrographs using NOVA NANO SEM 450 Scanning Electron Microscope (SEM). Two probe AC impedance measurements were made on pellets electroded with silver paint using Novo control Alpha-A High Performance Frequency Analyzer in the frequency range 1Hz - 1MHz and in the temperature range 200 – 700 ^{0}C in air. Impedance analysis has been used to separate contributions of grains, grain boundaries and electrode-specimen interface to the total observed resistance.

2. Results and discussion

Fig.1 shows DSC plot of ESB powder ash . DSC plots show three endothermic peaks. One is observed around 100 ^{0}C may be due to loss of adsorbed moisture and second peak is observed at 670 ^{0}C which corresponds to Face Cantered cubic Bi_2O_3 Phase formation which is very good ionic conductor [8-9] . The third endothermic peak corresponds to melting of ESB [9]. Fig.2 shows the XRD pattern of ESB sintered at 900 ^{0}C. XRD patterns have been indexed on the basis of fluorite structure similar to Bi_2O_3 using JCPDS file no 27-0052. Density of the sintered c pellets is found in the range 96-97%. This is due to sintering temperature (900 ^{0}C) close to melting temperature. Fig.3 shows the micrograph of thermally etched ESB sample. It can be seen from Fig.3 that the ESB nano grains are bonded to each other, showing very dense with negligible porosity irrespective of the low sintering temperature used in this process. Impedance measurements have been made in air in the temperature range 200-700 ^{0}C. Fig.4 shows the Nyquist plot of ESB at 200^{0}C, 300^{0}C, 400^{0}C and 500 ^{0}C. The intercept of the grain and grain boundaries arcs is the total resistance, R_t, of the ESB electrolyte. Total conductivity of the samples is given by following relation: $\sigma_t = \frac{L}{S \times R_t}$ where, σ_t is the total conductivity, R_t is the total resistance, L is the thickness and S is the area of the sample. ESB has the ionic conductivity value 3.5 S/m at 500 ^{0}C and it is higher than the value of 2.3 S/m observed in conventional sintered ESB prepared by solid state method [2,10].

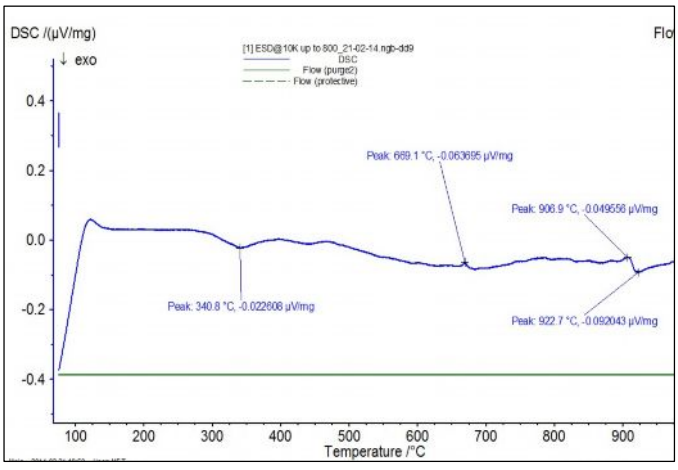

Figure.1 DSC plot of ESB powder

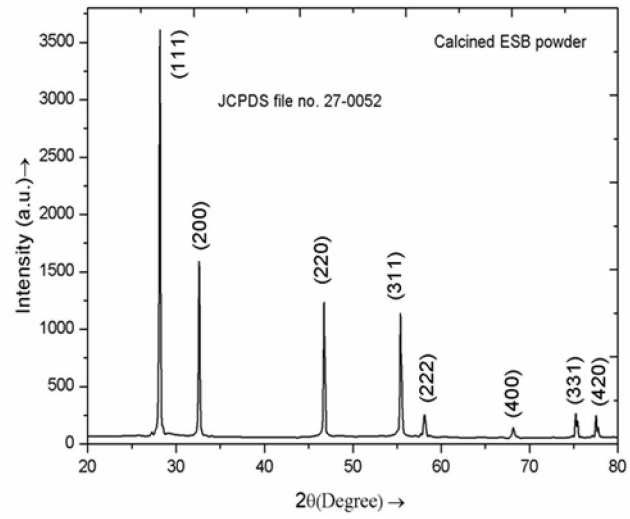

Figure.2 XRD pattern of sintered ESB sample

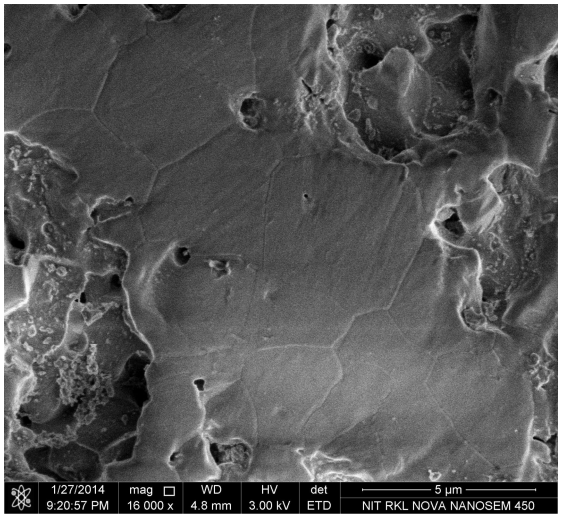

Figure.3 SEM micrograph of sintered ESB

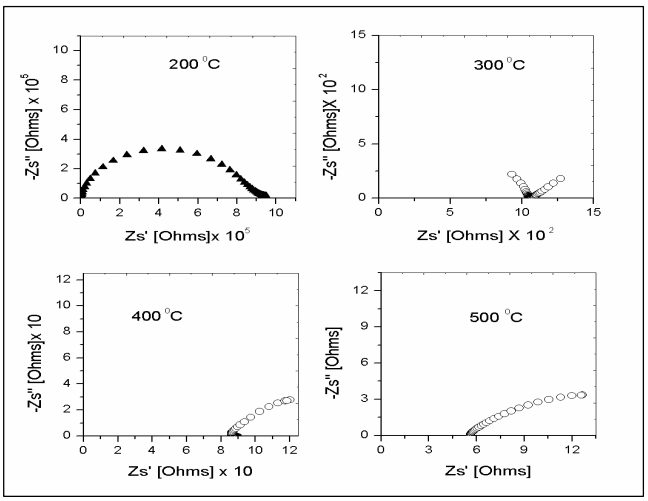

Figure.4 Impedance plot of ESB

3. References.

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