



## Structural and electrical properties of $\text{Bi}_3\text{Y}_{0.9}\text{W}_{0.1}\text{O}_{6.15}\text{-La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (BiYWO-LSM) composites



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### ARTICLE INFO

#### Keywords:

SOFc  
SOFc cathode  
Composite material  
Mixed ionic – electronic conductivity  
Transference numbers  
Bismuth oxide  
X-ray diffraction  
a.c. impedance spectroscopy

### ABSTRACT

Electrical conductivity and structural behavior in  $\text{Bi}_3\text{Y}_{0.9}\text{W}_{0.1}\text{O}_{6.15}\text{-La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  (BiYWO-LSM) composite cathodes for intermediate temperature solid-oxide fuel cells (IT-SOFCs) have been investigated. The ionically conducting component (BiYWO) was selected as it not only exhibits high oxide ion conductivity at intermediate temperatures, but also shows good long-term stability. The LSM component is a well-known electronic conductor, commonly used for SOFC cathodes and also shows high interfacial polarization effects. Both composite components exhibit similar thermal expansion coefficients. Composites of different molar ratios of components were prepared by sintering the components together at 850 °C. Electrical behavior was studied by a.c. impedance spectroscopy and transference number measurements were used to determine the ionic and electronic contributions to total conductivity. Percolation type behavior was observed for total conductivity and the percolation threshold value was determined to be in the bismuth rich region of the compositional range, due to the significant difference in the grain sizes of the two components. Ionic and electronic components of the total conductivity at, above and below the percolation threshold are discussed. Stability measurements on a composition close to the percolation threshold show some degree of conductivity decay on prolonged annealing at 650 °C, which is partly recoverable on heating to higher temperatures.

### 1. Introduction

Composite multi-phase materials are attracting increasing attention for a variety of applications, since they offer the possibility of designing new materials with tailored properties by simply combining two or more different constituents. One such application is in electrochemical devices, for example composites can be used as cathode materials in solid oxide fuel cells (SOFCs) [1–4]. The oxygen reduction reaction (ORR) in SOFCs occurs at the so called triple phase boundary (TPB), which is the point of contact between gaseous, ionically conducting and electronically conducting phases [5]. Ideally, cathode materials have high porosity and high values of both ionic and electronic conductivity, which enhances the extent of the TPB. This can be achieved in single phase materials such as LSCF ( $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ) and BSCF ( $\text{Ba}_{1-x}\text{Sr}_x\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ) [6,7], which show mixed ionic-electronic conduction. Multi-phase composite materials have also been considered in this role, with the advantage that the TPB can be extended to the bulk of the material, resulting in a significant reduction of polarization

resistance and hence increasing cell efficiency.

Apart from ceramic–metal (CERMET) composites [e.g. 8,9], ceramic–ceramic composite cathodes, involving one ceramic component of high ionic conductivity and another ceramic component of high electronic conductivity have also been studied. The ionically conducting component is typically a stabilized zirconia or doped ceria, while the electronic component is typically a perovskite, such as  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  [10,11]. Bismuth oxide based compounds are known for their exceptionally high oxide ion conductivity at relatively low temperatures [12,13] and would be interesting candidates for composite cathodes. Indeed, pure bismuth oxide exhibits the highest oxide ion conductivity of any known solid. While there has been concern over the use of bismuth oxide based materials in SOFCs, due to their ease of reduction under reduced oxygen partial pressures and poor stability, it has been demonstrated through careful chemical and engineering design, that these compounds can be used successfully in the construction of intermediate temperature solid oxide fuel cells (IT-SOFCs) [14,15].

In this paper a new composite material formed of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$

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and a stabilized  $\delta$ -bismuth oxide phase ( $\text{Bi}_3\text{Y}_{0.9}\text{W}_{0.1}\text{O}_{6.15}$ ) is presented and its electrical and structural properties characterized and discussed. The  $\text{Bi}_3\text{Y}_{0.9}\text{W}_{0.1}\text{O}_{6.15}$  composition has been chosen for the present study, because of its enhanced stability compared to other stabilized  $\delta$ -bismuth oxide phases [16], which show a degree of conductivity decay and structural changes on prolonged annealing at the working temperatures of IT-SOFCs. Tungsten doping into isovalent substituted bismuth oxides has been shown to impart greater stability in these systems [17,18].

## 2. Experimental

### 2.1. Sample preparations

$\text{Bi}_3\text{Y}_{0.9}\text{W}_{0.1}\text{O}_{6.15}$  (BiYWO) was prepared by solid-state reaction of the parent oxides. Stoichiometric amounts of  $\text{Bi}_2\text{O}_3$  (Sigma Aldrich, 99.9%),  $\text{Y}_2\text{O}_3$  (Sigma Aldrich, 99.99%) and  $\text{WO}_3$  (Sigma Aldrich, 99.99%) were ground in ethanol using a planetary ball mill for ca. 12 h. The dried mixture was heated in air at 700 °C for 24 h, then cooled and reground in an agate mortar. The sample was then heated at 750 °C for 24 h and quenched to room temperature.  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  (LSM) was prepared using a glycine-nitrate method with  $\text{La}(\text{NO}_3)_3$ ,  $\text{Sr}(\text{NO}_3)_2$  and  $\text{Mn}(\text{NO}_3)_2$  as precursors following the procedure presented by Tsai et al. [19].

BiYWO and LSM were mixed at various volume ratios ( $0 \leq f \leq 1$ ), defined by the parameter  $f = \frac{\text{BiYWO phase volume}}{\text{composite volume}}$ , where the phase volume was based on the crystallographic density derived by Rietveld analysis and the composite volume was a weighted sum of the individual phase volumes. The mixtures were ground together in an agate mortar in acetone with a drop of polyethylene glycol 400, dried and pelletized. Pellets were pressed isostatically at a pressure of 400 MPa and heated to 850 °C for 10 h. Sample density was measured by the Archimedes method in isobutanol and compared with the theoretical crystallographic density, derived by Rietveld analysis, for the relative density determination.

### 2.2. Electrical measurements

Electrical parameters were determined by a.c. impedance spectroscopy up to ca. 800 °C, using a fully automated Novocontrol alpha-N frequency response analyzer, in the frequency range 0.1 Hz to  $2 \times 10^7$  Hz. Samples for impedance measurements were prepared as rectangular blocks (ca.  $8 \times 3 \times 3$  mm<sup>3</sup>) cut from quenched sintered pellets using a diamond saw. Platinum electrodes were sputtered by cathodic discharge on the two smallest faces. Impedance spectra were acquired over two cycles of heating and cooling at stabilized temperatures. Impedance at each frequency was measured repeatedly until consistency (2% tolerance in drift) was achieved or a maximum number of three repeats had been reached, using an algorithm described earlier [20].

The total conductivity of the  $f = 0.81$  sample, as measured by a.c. impedance spectroscopy, was monitored during long-term isothermal annealing at 650 °C in 50 min intervals for ca. 210 h. To minimize electrode degradation during long-term annealing [21,22], sputtered gold electrodes were used.

The ionic and electronic contributions to the total conductivity were measured using a modified EMF method, with an external adjustable voltage source in the concentration cell  $\text{O}_2(\text{pO}_2 = 1.01 \times 10^5 \text{ Pa})$ : Pt | sample | Pt:  $\text{O}_2$  ( $\text{pO}_2 = 0.2095 \times 10^5 \text{ Pa}$ ), as described in detail elsewhere [23]. Measurements were performed on cooling between ca. 800 °C and ca. 500 °C at stabilized temperatures for selected composites ( $0.75 \leq f \leq 1$ ).

### 2.3. Diffraction

X-ray powder diffraction (XRD) data were obtained on a Philips X'Pert Pro diffractometer fitted with an X'Celerator detector, using Ni filtered  $\text{Cu-K}\alpha$  radiation ( $\lambda_1 = 1.54056 \text{ \AA}$  and  $\lambda_2 = 1.54439 \text{ \AA}$ ). Data were collected in flat plate  $\theta/\theta$  geometry and calibrated against an external  $\text{LaB}_6$  standard. Room temperature data suitable for detailed Rietveld refinement were collected in the  $2\theta$  range 5–105°, in steps of 0.0167°, with an effective scan time of 400 s per step. Elevated temperature measurements were made using an Anton Paar HTK-1200 N camera. Samples were mounted on a Pt coated ceramic sample holder and data collected in steps of 50 °C, from 50 °C to 850 °C, in the  $2\theta$  range 5–105°, with a step width of 0.0334° and an effective scan time of 50 s per step. Unit cell parameters were determined by Rietveld analysis using the GSAS suite of programs [24]. A cubic model in space group  $Fm\bar{3}m$  was used for all refinements of the BiYWO phase [20]. Refinement of the LSM phase was carried out using the structure reported by Pinsard et al. in space group  $Pbnm$  [25].

### 2.4. Morphology and thermal analysis

Morphological characterization of prepared samples was carried out with a Raith e-Line plus scanning electron microscope. Combined differential thermal analysis and thermogravimetric analysis (DTA/TGA) was carried out using a TA Instruments Q600. Approximately 30 mg of powdered sample in an alumina crucible was monitored over heating and cooling cycles, between ambient temperature and 1000 °C, at a heating rate of 20 °C min<sup>-1</sup> in flowing air.

## 3. Results and discussion

### 3.1. Composite structure

Room temperature XRD patterns for the studied BiYWO-LSM composites are presented in Fig. 1a. In the composition range  $0.6 \leq f \leq 1$ , diffraction patterns show a simple mixture of individual BiYWO and LSM phases, with no evidence of additional phases. For the LSM rich composites ( $f < 0.6$ ), a small amount of an additional rhombohedral phase is visible. The diffraction peaks of this phase show a good match to those of  $\text{Bi}_{0.775}\text{La}_{0.225}\text{O}_{1.5}$  (BLO, PDF No. 00-048-0346). However, since this phase is part of a solid solution in the  $\text{Bi}_2\text{O}_3$ - $\text{La}_2\text{O}_3$  system [26,27], its exact stoichiometry cannot be stated unambiguously. Moreover, since an isostructural phase is known to occur in the  $\text{Bi}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$  system [28], one cannot exclude the possibility that this is a bismuth yttrate phase or even a mixed yttrate/lanthanate phase. It is likely that this phase occurs at the BiYWO/LSM interface, but there is no direct evidence for this in the SEM images. Growth of interfacial secondary phases is seen in other composite materials, for example in the LSM-YSZ (yttria-stabilized zirconia) composite, where  $\text{La}_2\text{Zr}_2\text{O}_7$  and  $\text{SrZrO}_3$  phases are observed at the YSZ/LSM interface [4].

Fig. 1b shows the compositional variation of unit cell volume for the BiYWO and LSM phases. It can be seen that the unit cell volume of the BiYWO phase increases with increasing  $f$  value up to around 0.75, above which the volume remains fairly constant. This indicates that the BiYWO phase is Bi poor at low values of  $f$ , consistent with partial reaction of the BiYWO phase to form BLO at these compositions. Above  $f = 0.75$  the constant volume of the BiYWO phase suggests no significant reaction between BiYWO and LSM as evidenced by the X-ray diffraction data.

The thermal variation of unit cell volume for the BiYWO and LSM phases in a representative composite ( $f = 0.81$ ) is shown in Fig. 2, with similar plots obtained for other  $f$ -value composites. It can be seen that the two plots are virtually parallel suggesting good matching of thermal expansion for the two component phases. At about 550 °C the plots show a change in slope, with the volumes at higher temperatures slightly larger than predicted by a simple linear extrapolation of the low

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