Journal of Alloys and Compounds 505 (2010) 592–597

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Electrical, optical and photoelectrochemical properties of $BaSnO_{3-\delta}$ Applications to hydrogen evolution

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ARTICLE INFO

Article history:
Received 22 March 2009
Received in revised form 12 June 2010
Accepted 16 June 2010
Available online 25 June 2010

Keywords:
Electrode materials
Hetero-junction
Semiconductors
Grain boundaries
X-ray diffraction
Electrochemical reactions

ABSTRACT

Photoactive $BaSnO_{3-\delta}$ is synthesized at 1253 K under air free atmosphere. The oxygen deficiency leads to a concomitant reduction of Sn^{4+} ions and the transport properties suggest low lattice polaron conduction with activation energy of 0.16 eV. Above 445 K, a plateau region is observed in the thermal variation of the conductivity caused by oxidation process, i.e. oxygen capture. The absence of the electrochemical peak $Sn^{2+/4+}$ in the intensity-potential curve corroborates the delocalization of the stereo chemical pair Sn^{2+}: $5s^2$. From photoelectrochemical measurements, the band gap is 2.80 eV and the transition is directly allowed. Moreover, indirect transition occurs at 2.60 eV. The material exhibits a long-term chemical stability over the whole pH range. In KOH (0.5 M) solution, the semi-logarithmic plot gave a current density of 24 $\mu A\,cm^{-2}$ and a corrosion potential of $-0.447\,V_{SCE}$. The capacitance measurements and cyclic voltammetry indicate that the photoresponse of $BaSnO_{3-\delta}$ is characteristic of n-type conductivity with a flat band potential of $-0.87\,V_{SCE}$ and an electron density of $1.2 \times 10^{20}\,cm^{-3}$. The best quantum efficiency occurs at 400 nm and is attributed to a depletion width (15 nm) and a diffusion length (57 nm) compared to a large penetration depth (820 nm). The electrochemical impedance spectroscopy (EIS) reveals the presence of bulk contribution effect and the Nyquist response has been decomposed on R–C parallel circuit. As application, $BaSnO_{3-\delta}$ has been tested successfully for the hydrogen evolution under visible illumination when combined with the delafossite $CuFeO_2$ as sensitizer.

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1. Introduction

The perovskites $ASnO_3$ in which A is commonly an alkaline earth are important sensor materials to detect various gases [1]. They have also been studied for possible applications of the light-to-electrical and/or chemical energy conversion [2], stable capacitors [3] and oxygen-permeable ceramic membranes [4]. $BaSnO_3$ is classified as a wide band gap semiconductor where the conduction band (CB), originating from σ anti bonding mixture of Sn: 5s-O^{2-}: 2p orbital, is separated from the broad valence band (VB) of anionic O^{2-}: 2p parentage by a gap exceeding 3 eV [5]. It is well established now that the transport properties of stannates can be significantly improved by either doping on both A- and Sn-sub lattices [6] with heterovalent ions or by oxygen deficiency [7]. The electrical conductivity changes considerably when heated under low oxygen partial pressure due to the redox equilibrium with the surrounding atmosphere. Electrons are dominant carriers in the perovskites and the oxide represents a valence compensated system where oxygen extraction from the crystal lattice occurs concomitantly with tin reduction [8]. Consequently, $ASnO_3$ are n-type semiconductors and increasing the unit cell (Ca → Ba) enhances the mobility of oxygen ions and the degree of reduction [9]. The electrical studies reported on $BaSnO_3$ so far have been limited to low temperatures, a transition occurs from hopping mechanism to a conduction governed by activation to the mobility edge [10]. The scattering is so small that the hopping occurs through equivalent sites with almost free carriers and activationness energy. The conduction occurs via adiabatic hops of low polaron and the increase of the conductivity reflects an enhancement in the mobility. In the solid solution $Ba_{1-x}La_xSnO_3$, the thermo electric power indicated that there is more charge carriers than that would follow nominal valence and this is due to oxygen vacancies [11]. However, the data at high temperatures are missing and to our knowledge, no studies have been dealt in this direction.

On the other hand, there have been many investigations aimed to improve the efficiency of wide band semiconductors in photoelectrochemical (PEC) devices. Most materials used for the water splitting are based mainly on titanium oxides. So, it seemed attractive to develop new active materials for PEC conversion. The oxides containing cations with nd^{10} configuration are among the most sta-

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doi:10.1016/j.jallcom.2010.06.081

ble materials in photoelectrochemistry. In order to have a large band bending at the interface semiconductor/electrolyte, i.e. an efficient charge separation of electron/hole (e^-/h^+) pairs, the junction electric field must be large [12]. This requirement supposes the electron affinity of the semiconductor to be as low as possible. In this optic, barium should decrease the electron affinity of $BaSnO_3$ and shifts the flat band potential cathodically. In addition, $BaSnO_3$ is no toxic and chemically long lived. These characteristics make it attractive for the solar energy conversion [13]. However, it suffers from the drawback of low quantum efficiencies resulting from the large gap absorbing the UV radiations which entails only 5% of the sunlight. The hetero-junctions allow the extension of the spectral photoresponse toward the visible region. Therefore, the main aim of the present work was the PEC characterization of deficient stannate $BaSnO_{3-\delta}$ to assess its photoactivity for the hydrogen production. The importance of hydrogen, as sustainable and clean energy, has been highlighted in the literature [14]. We have coupled the chemical stability of $BaSnO_{3-\delta}$ with the absorbance of the delafossite $CuFeO_2$ while attempting to provide photoelectrons with enough reducing ability to reduce water into hydrogen. $CuFeO_2$ is selected because of its low cost, small optical gap and chemical stability [15].

2. Experimental

$BaSnO_3$, prepared by solid state ceramic method [16], served as starting material for further heat treatment. Appropriate amounts of $BaCO_3$ (Prolabo, 99%) and prefired SnO_2 (Ventron, 99.9%) were homogenized in an agate mortar for 30 nm. The powder was cold pressed into pellets under uniaxial pressure of 5 kbar. The pellets were fired at 1323 K for 48 h in air after which they were reground and refired for a further 36 h to get a well-crystallized oxide. Reduction was achieved by sealing $BaSnO_3$ pellets in silica ampoule under low pressure (<1 mbar) and firing at 1253 K (10 K min^{-1}) overnight. The process was speeded up considerably when small amount of Fe was used as getter. $CuFeO_2$ powder has been synthesized by nitrate route as reported in our previous work [15]. The control of the phases purity and the refinement of the lattice constants were performed with X-ray diffraction (XRD) at a scan speed of 0.05° min^{-1} in the 2θ range (5–80°) using monochromatized Cu Kα radiation.

Care was taken to minimize contacts resistance. Silver past was deposited on both sides of the pellet and the electrical conductivity was measured by the standard two probe technique. The thermoelectric power (type of conductivity) was performed by the differential technique with a temperature gradient of ~10 K through the pellet. The thermo emf was measured with a digital micro voltmeter (Tacussel, Aris 20000, impedance 10^{12} Ω) while the temperature gradient was determined with a thermo couple (type K).

Copper wires were soldered on one face of the pellets with silver paint; the pellets were assembled in glass holders with insulating epoxy resin leaving a geometrical surface of 0.2 cm^2. A standard three-electrode cell has been used for PEC characterization: the working electrode, an auxiliary Pt cathode (1 cm^2) and a saturated calomel electrode (SCE) to which all the potentials were quoted. The intensity-potential $J(V)$ characteristics and the capacitance curves were plotted thanks to a Voltalab PGZ 301 potentiostat/galvanostat (Radiometer). The electrode was irradiated through a quartz window with a 500 W Xenon lamp whose output was passed trough a monochromator with 10 nm band pass. The light intensity was measured at each wavelength with a calibrated light-meter (Testo 545) placed at the same position of the electrode. The aqueous solution containing KOH (0.5 M) as supporting electrolyte was continually flushed with nitrogen. The capacitance was measured as a function of the potential with a rate of 10 mV step AC voltage signal at a frequency of 10 kHz and 10 mV peak to peak in magnitude. The complex impedance data were acquired using small amplitude wave signals through a frequency response analyzer in the frequency range (10^{-3}–10^5 s^{-1}) with ten points per decade.

The photocatalytic tests were carried out in a closed gas circulation equipped with a water cooled double walled reactor previously described in detail [17]. The reactor was placed in a fixed position to keep a constant light flux. The temperature was regulated by a thermo stated bath regulated at 323 ± 2 K. The light source consists of three tungsten lamps (200 W) providing 2.09×10^{19} photons s^{-1} and the powder was dispersed by magnetic stirring under constant agitation. Prior each run, the solution (Na_2SO_4, 10^{-2} M) was purged for 35 min with pure nitrogen. Hydrogen in the outgoing gas was identified by gas chromatography; the amount was evaluated volumetrically by means of a graduated burette and corrected from blank experiments. The solutions were prepared from reagents of analytical quality and twice distilled water.

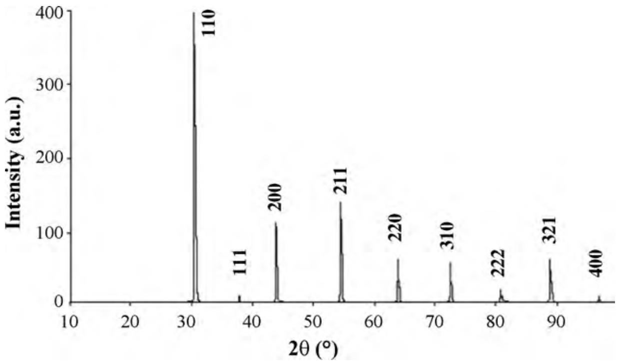

Fig. 1. XRD pattern of $BaSnO_{3-\delta}$ elaborated in silica tube.

3. Results and discussion

$BaSnO_{3-\delta}$ exhibits a blue color and the XRD pattern (Fig. 1) is indexed in a cubic unit cell as evidenced from the tolerance factor t (1.01: considering Shannon ionic radii). The lattice constant $\{a = 0.4117(2)\,\text{nm};\ \}$ is slightly larger than that of $BaSnO_3$ $\{0.4115(3)\,\text{nm}\}$; this implies an increase of the unit cell volume ($\Delta V = 0.0698\,\text{nm}^3$) induced by the oxygen under-stoichiometry. This is attributed to a small amount of Sn^{2+} ($r_{Sn^{2+}} = 0.110\,\text{nm}$) in six-fold coordination [18], generated by a charge compensation mechanism, smaller than Sn^{4+} ($r_{Sn^{4+}} = 0.110\,\text{nm}$). The materials with a Jahn–Teller ion bearing a lone pair like Sn^{2+} or Sb^{3+} crystallize in distorted structures with a low coordination environment and a limited composition range unless the lone pair ns^2 is delocalized in CB [19]. Under strong reducing atmosphere (H_2/Ar: 1/9), $BaSnO_3$ converts into SnO and β-Sn as proven by XRD and optical microscopy.

3.1. Transport properties

The high temperature defect chemistry of oxides and mechanism of transport properties have been well investigated in the past. In $BaSnO_3$, the ions Sn^{4+} occupy octahedral sites while Ba^{2+} are located in dodecahedrons and the perfect oxide is white and exhibits an insulating behavior [20,21]. The conductivity (σ) is extremely low and could not be measured, it can be assumed to be less than $10^{-8}\ \Omega^{-1}\,\text{cm}^{-1}$. However, σ is significantly increased by oxygen deficiency caused by equilibration under low oxygen partial pressure; the presence of iron (getter) lowers the partial oxygen pressure down to 10^{-6} atm. The system is electrically neutral and the formation of anionic vacancies occurs with Sn^{4+} reduction whose associated energy levels lie below the bottom of CB:

$$BaSnO_3 \rightarrow BaSn^{4+}_{1-\delta/2}Sn^{2+}_{\delta/2}O_{3-\delta} + 2\delta[e^-(CB)] + \delta/2O_2 \qquad (1)$$

The conduction occurs by electron hopping through mixed $Sn^{4+/2+}$ions located in octahedra sharing common corners. The thermal variation $\sigma(T)$ indicates semi conducting behavior with a positive temperature coefficient, i.e. σ increases with increasing T and the data are well fitted by a polaron model: $\sigma = \sigma_o \exp -(\Delta E/kT)$ (Fig. 2, Inset), the pre-exponential constant σ_o is temperature independent. The activation energy ΔE ($0.16\,\text{eV} \ll 0.5E_g$), i.e. the separation between the Fermi level and CB, rules out any intrinsic conductivity. Consequently, the variation $\sigma(T)$ should result from a thermal activation of electrons, localized at the Fermi level. The released electrons are captured by Sn^{4+} ions to yield Sn^{2+} which act as donors shallows in conformity with n-type conductivity. This is explained in term of oxygen vacancies in accordance with the Kröger–Vink notation when the oxide is heated under oxygen free

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