Materials Science in Semiconductor Processing 29 (2015) 283–287

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Physical characterization of the semiconducting deficient perovskite $BaSnO_{3-\delta}$

B. Hadjarab, M. Trari, M. Kebir*

Laboratory of Storage and Valorization of Renewable Energies (USTHB, Faculty of Chemistry) B.P. 32 Algiers, 16111, Algeria

ARTICLE INFO

Available online 20 May 2014

Keywords:
Stannate
Electrical properties
Photo-electrochemical
Variable range hopping

ABSTRACT

The semiconducting stannate $BaSnO_{3-\delta}$, prepared in evacuated silica ampoule, crystallizes in a cubic perovskite structure. The magnetic susceptibility (less than 2×10^{-5} emu cgs mol^{-1}) is due to itinerant electrons. The conductivity obeys to an exponential law $\sigma_o \exp(-E_a/kT)$ with activation energy of 3 meV and electrons hopping between mixed valences $Sn^{2+/4+}$. A variable range hopping is predicted from the non linear behavior of the plot ln (σ) versus T^{-1}. At high temperatures, the conductivity follows a thermally activated hopping of lattice polaron with activation energy of 0.17 eV. The plot deviates from the linear behavior due to the oxidation of $BaSnO_{3-\delta}$; the fully oxidized specimen is restored at 578 K in air. The thermal variation of the thermopower suggests a finite density of states at the Fermi level. The semiconducting properties are elucidated from the photo-electrochemical characterization. The Mott–Schottky plot in alkaline medium shows a straight line from which an electron density of 3.07×10^{21} cm^{-3}, a flat band potential of -0.375 V_{SCE} and a space charge region of 2.3 Å have been determined.

1. Introduction

Over the last decade, there has been a renewed interest in the ternary systems A–B–O where A is commonly an alkaline earth and B a post transition metal (=Sn or Pb) [1–3]. ABO_3 crystallizes in the perovskite structure typified by the mineral $CaTiO_3$ and have found many applications in electronic, optoelectronic [4] and dielectric devices [5]. Increasing the unit cell of $ASnO_3$ enhances the mobility of oxygen and in this way the degree of reduction according to the following sequence: $CaSnO_3 \rightarrow SrSnO_3 \rightarrow BaSnO_3$. The transport properties range from metallic behavior ($BaPbO_3$) [6] to insulating one ($CaSnO_3$). Therefore, a pertinent question arises: does the resistivity of stannates decrease without affecting significantly the optical transmittance. In wide band gap semiconductors (SC_s), the optical transparency combined to an electronic conductivity requires generation of electron degeneracy by a suitable doping and/or oxygen deficiency and such conditions can be easily obtained with alkaline earth stannates [7]. $BaSnO_3$ is transparent in the visible region and is at the limit of the insulating-metal transition; a substitution of as little as 0.01 La^{3+} onto the A sub lattice changes significantly the transport properties [8]. This occurs because of the low density of states where the Fermi level (E_f) moves above the mobility edge to extended states. However, the open question with such oxides remains the absence of superconductivity in spite of the existence of tin accommodated in mixed valence states as required by the electro neutrality and why is the critical temperature (T_C) so low in $BaPbO_3$ [9]; the answer is partially highlighted by the metal–oxygen bond through the overlap of the B^{4+}: ns–O: 2p orbital [10]. This can be inferred to the energy difference between Sn: 5s and Pb: 6s (~1.4 eV) leading to a more ionic Sn−O bond. In $BaSnO_3$, the valence band (VB) is made up from O^{2-}: 2p orbital separated from a

* Corresponding author. Tel.: +213 21 24 79 58; fax: +213 21 24 80 08.
E-mail address: medkebir@yahoo.fr (M. Kebir).

http://dx.doi.org/10.1016/j.mssp.2014.04.041
1369-8001/

conduction band (CB) of hybridized Sn: 5s/O^{2-}: 2p by a forbidden band (E_g) of ~3 eV [11].

The electrons are introduced by oxygen extraction from the crystal lattice and the electron effective mass decreases as the impurity band merges with the conduction band. Indeed, the physical properties of deficient oxides with mixed valences metal are governed by the oxygen partial pressure [9]. The vacancies produce a random potential on the extra electrons and the non-linear dependence of the conductivity at low temperatures indicates a variable range hopping (VRH) as evidenced from the plot ln (σ) vs. $T^{-0.25}$ [12]. VRH involves hopping over large distances rather than between nearest neighbors. The electrical studies of $BaSnO_{3-\delta}$ are limited to room temperatures whereas the thermo electric data at high temperatures are missing. The present paper covers the synthesis and the determination of optical and electrical properties of *n*-type $BaSnO_{3-\delta}$.

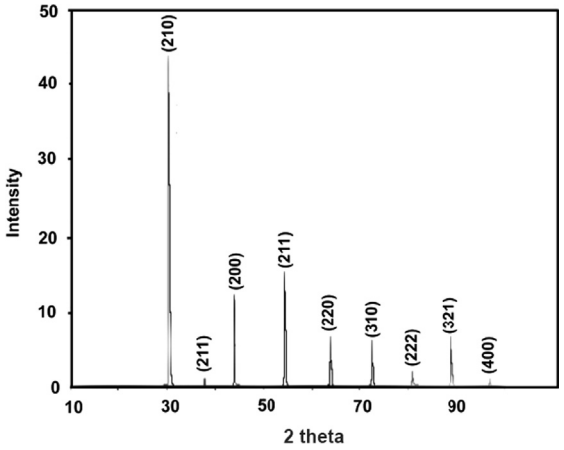

Fig. 1. XRD pattern (CuKα irradiation) of $BaSnO_{3-\delta}$ synthesized in evacuated silica tube.

2. Experimental

$BaSnO_3$, prepared by solid state reaction, served as starting material for further heat treatment. Appropriate amounts of $BaCO_3$ and dried SnO_2 both of purity (> 99.5%) were homogenized in a agate mortar and calcined at 1040 °C for 48 h after which the powder was reground, pressed into pellets (∅=13 mm) under 5 kbar and reheated for 36 h to get a well crystallized oxide. The reduction was achieved by sealing $BaSnO_3$ pellets in silica ampoules under low pressure (< 1 mbar) and firing at 980 °C. The process was speeded up considerably when a small amount of Fe was used as a getter.

X-ray diffraction was carried out at a scan speed of 0.05° min^{-1} in the 2θ angle range (10–100°) using monochromatized Cu Kα radiation. The lattice constants were refined from corrected *d*-values by the least square method using Si as standard. The density has been determined by the hydrostatic method, comparison between theoretical and experimental densities gave a compactness of 95%. The magnetic susceptibility (χ) of $BaSnO_{3-\varepsilon}$ was recorded down to liquid helium temperature in a magnetic balance under a field of 20,000 G. The χ (T) values were corrected by subtracting the core diamagnetism of relevant ions [13].

The d.c. conductivity (σ) measurements were done on sintered pellets over the range (4.2–750 K) using the four probe technique. The thermopower (S) is well representative for the characterization of generated vacancies and was measured in home hold equipment. All temperature measurements were referenced to a digital calibrated chromel–alumel thermocouple (type K) and are accurate to ~ ± 1 K. The small heat conductivity of $BaSnO_3$ made it possible to use large gradient temperatures down to 4 K. $BaSnO_{3-\delta}$ exhibits an excellent chemical stability; it is insoluble even in $HClO_4$ or aqua regia and the off stochiometry cannot be detected chemically. However, the δ-value can be determined indirectly via the electrons density $N_D(=\delta/2)$ using the Mott–Schottky relation. In this respect, the capacitance measurements were performed in KOH electrolyte with a PGZ 301 Voltalab potentiostat, the frequency was set at10 ks^{-1}.

3. Results and discussion

3.1. Characterization of $BaSnO_{3-\delta}$

$BaSnO_{3-\delta}$ exhibits a light blue color and the XRD pattern, shown in Fig. 1, is indexed in a cubic symmetry. The lattice constant {a=0.4117(2) nm} is slightly larger than that of $BaSnO_3$ {0.4115(3) nm}. This is attributed to the presence of a small amount of Sn^{2+}, generated by a charge compensation mechanism, with a radius (r_{Sn2+} = 0.110 nm)[1] smaller than that of Sn^{4+} (r_{Sn4+}=0.069 nm) in octahedral coordination [14]. The experimental density (=6.941 g cm^{-3}) agrees with that calculated on the base of one formula unit per unit cell (7.231 g cm^{-3}). Generally, the oxides bearing a stereo chemical inert electron pair (Sn^{2+}, Pb^{2+} or Sb^{3+}) crystallize in distorted structures with a low coordination environment and a limited composition range unless the lone pair is delocalized in the conduction band. Under strong reduction (H_2/Ar: 1/9), $BaSnO_3$ decomposes irreversibly into SnO and β-Sn as shown from XRD and optical microscopy.

The thermal variation of the magnetic susceptibility χ (T) of $BaSnO_{3-\delta}$ (Fig. 2) is positive and nearly temperature-independent down to 30 K; the sharp upturn which might be due to localized paramagnetic centers. Electron paramagnetic resonance, carried out on the starting SnO_2, has shown that they were Fe^{3+} ions, easily detected because of the dilution effect. The weak temperature dependence of the susceptibility is ascribed to collective electrons (singlet polarons). Taking into account the diamagnetic orbital contribution, the paramagnetic term of itinerant

[1] The radius of cations with lone pair of electrons such Sn^{2+}, Pb^{2+} or Sb^{3+} are not accurate and the values of the literature are somewhat variable.