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Synthesis, physical and photo electrochemical characterization of La-doped SrSnO₃

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Abstract

The transport properties of $Sr_{0.98}La_{0.02}SnO_{3-\delta}$ in the system $Sr_{1-x}La_xSnO_{3-\delta}$, after which the pyrochlore $La_2Sn_2O_7$ appears, were investigated over the temperature range 4.2–300 K. The oxide was found to be n-type semiconductor with concomitant reduction of Sn^{4+} into Sn^{2+} . The magnetic susceptibility was measured down to 4.2 K and is less than 3×10^{-5} emu cgs mol⁻¹ consistent with itinerant electron behavior. The electron is believed to travel in a narrow band of Sn:5s character with an effective mass $\sim 4m_0$. The highest band gap is 4.32 eV and the optical transition is directly allowed. A further indirect transition occurs at 4.04 eV. The electrical conductivity follows an Arrhenius-type law with a thermal activation of 40 meV and occurs by small polaron hopping between nominal states $Sn^{4+/}$. The linear increase of thermo-power with temperature yields an electron mobility $\mu_{300 \text{ K}}$ ($2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) thermally activated. The insulating-metal transition seems to be of Anderson type resulting from random positions of lanthanum sites and oxygen vacancies. At low temperatures, the conduction mechanism changes to a variable range hopping with a linear plot $Ln \rho^{-1}$ vs. T^{-4} . The photo electrochemical (PEC) measurements confirm the *n*-type conductivity and give an onset potential of $-0.46 V_{\text{SCE}}$ in KOH (1 M). The Mott–Schottky plot $C^{-2}-V$ shows a linear behavior from which the flat band potential $V_{\text{fb}} = +0.01 V_{\text{SCE}}$ at pH 7 and the doping density $N_{\text{D}} = 1.04 \times 10^{21} \text{ cm}^{-3}$ were determined.

Keywords: A. Oxides; C. X-ray diffraction; D. Transport properties; D. Electrochemical properties; D. Phase transitions

1. Introduction

The stannates $ASnO_3$, where A denotes an alkaline earth or II_B elements, exhibit interesting physical properties many of which are associated with impurities in the crystal lattice [1]. They have gained increasing interest owing to their technical applications in the field of humidity sensors [2,3], thermally stable capacitors [4] and electronic devices [5]. Despite such worthwhile features, only few investigations have been devoted to SrSnO₃ and to our knowledge, the transport properties have not been reported. In addition, the photo electrochemical (PEC) characterization does not form the subject of any previous study in contrast to homologous titanates. Increasing the unit-cell size of the stannate increases the mobility of oxygen ions and in this way, the degree of reduction $(CaSnO_3 \rightarrow SrSnO_3 \rightarrow BaS-nO_3)$. While $CaSnO_3$ remains colorless when heated in air free atmospheres with an electrical resistivity $\rho_{300 \text{ K}} > 10^7 \Omega \text{ cm}$, $BaSnO_3$ turns to blue due to an increase of oxygen vacancies followed by formation of delocalized Sn^{2+} . SrSnO₃ is white, poorly insulating and crystallizes in an ideal perovskite structure. It is transparent in the visible region and up to the near UV. The electrical conductivity may be enhanced either by substitution with suitable cations [6,7] or by deviation from the stoichiometry caused by equilibration under low oxygen partial pressure [8]. In both cases, the electron exchange takes place between mixed valent tin ions arranged in octahedral sites.

 $SrSnO_3$ is a large band gap semiconductor (SC) in which the valence band (VB) is made up from $O^{2-}:2p$ orbital separated from a conduction band (CB) of hybridized $Sn:5s/O^{2-}:2p$ by a forbidden band (E_g) exceeding 3 eV. Little is known about this oxide which was chosen because

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it is possible to modify the electronic configuration of tin by substitution of higher valent cation such as rare earths onto the A-sublattice. To preserve the electroneutrality, Sn^{4+} ions are reduced to Sn^{2+} and this change in ionization gives rise to an alteration of the color and an enhancement of the transport properties. The metal-nonmetal transition is attributed to random potential introduced by La³⁺-substitution and/or oxygen vacancies. At low temperatures, a variable range hopping (VRH) results from the nonlinear dependence of $\log (resistivity)^{-1}$ against reciprocal temperature [9]. Stannates are interesting materials for characterization from the physical and chemical point of view. The present paper deals with the synthesis and the improvement of the knowledge of optical and electrical properties of n-type SrSnO₃. The first results of PEC measurements are also presented. The material is not successful as anode in PEC devices because of the wide forbidden band and the weak value of the flat band potential $(V_{\rm fb})$ due to the large electron affinity (EA) of tin. Its possible application as optical coating is suggested.

2. Experimental

The limit composition $Sr_{0.98}La_{0.02}SnO_{3-\delta}$ was prepared by conventional solid state reaction from stoichiometric amounts La_2O_3 , SnO_2 (both of purity >99.9%), SrO and SnO. The starting oxides were intimately mixed in an agate mortar, pressed under 2 kbar into pellets ($\emptyset = 13 \text{ mm}$, thickness \approx 1 mm) and sealed in evacuated silica ampoules under low pressure (<1 Pa). The ampoules were heated at 1273 K for 15h and then water quenched. The same procedure was repeated twice in order to get homogeneous oxide. Excellent β -SnO was obtained by extended heating of aqueous solution of tin (II) chloride. SrO was prepared from SrCO₃ by thermal decomposition at 1173 K overnight whereas La₂O₃ was heated at 1173 K just prior use and introduced in a glove box. Pure SrSnO₃ was synthesized by solid reaction from SrCO₃ and dried SnO₂. Pellets were cold pressed and calcined to decompose carbonate at 1173 K overnight before regrinding and firing at 1473 K for 24 h. The products were handled in an argon dry box because of their strong moisture sensitivity. The X-ray diffraction (XRD) patterns of end products were carried out with a monchromatized Cu Ka radiation. Data were collected in steps of $0.02^{\circ} \text{min}^{-1}$ over a range from 5° to 100° (2 θ). The lattice constants were refined from the leastsquares method of the powder XRD data using Si as standard. The experimental density d_{exp} was measured by the hydrostatic method in toluene, known for its wetting properties. The relative density of the ceramic pellet $(= d_{exp.}/d_{theo.})$ approximates 94%, $d_{cal.}$ is the calculated density (from XRD). The optical absorption spectrum was obtained by the double beam method using a Jasco ratio recording spectrophotometer (V-530) equipped with an integrating sphere. The magnetic susceptibility data $\chi(T)$ were recorded down to liquid helium temperature thanks to a magnetic balance under a field of 0.18 T and corrected by subtracting the orbital diamagnetism from ions cores of relevant ions [10].

The electrical resistivity (ρ) was measured on sintered pellets using an automatic four-probe d.c. method. Electrical contacts of less than 2Ω resistances were established by soldering silver cement onto the sides of pellets. The thermoelectric power (S) data were obtained down to 4.2 K using a closed cycled helium cryostat. It should be noted that the precision of measurement is strongly dependent on the quality of thermal contact between the Cu blocks and the sample. The temperature difference across the sample was controlled by a digital calibrated chromel-alumel thermocouple (type K). S is defined as the proportionality constant between temperature gradient and induced electric potential emf (= $\Delta V/$ ΔT). emf was measured by a differential electrometer (Tacussel ARIES 20000) with an input impedance $Z_i = 10^{12} \Omega$.

Copper wires were attached on the backside of pellets with silver paint and mounted in appropriate glass holders using insulating paraffin wax. The electrochemical measurements were carried out under potentiostatic conditions using a three-electrode set up with a large area platinum counter electrode and a saturated calomel electrode (SCE) to which all potentials were referenced. An inert atmosphere was maintained by flushing ultrapure nitrogen in KOH (1 M) solution. The electrode potentials and capacitance measurements were monitored by a PGP 40 Radiometer potentiostat. A 800W halogen lamp was used as light source and equipped with a water filter to remove the heating effects. The photon flux reaching the electrode surface has been determined by a light meter (Testo 545) placed at the same position as the electrode. All the reagents were A.R. grade and the solutions were made up with twice distilled water.

3. Results and discussion

The XRD pattern of $La_{0.98}Sr_{0.01}SnO_3$, depicted in Fig. 1, is virtually free from reflections due to either starting oxides or other known tin (IV) phase. It indicates the



Fig. 1. XRD pattern of $Sr_{0.98}La_{0.02}SnO_3$ synthesized under O_2 free atmosphere.

formation of homogeneous single phase, which retains the cubic structure. The oxide has noticeably narrow peaks and therefore is well crystallized. The solid solution $Sr_{1-x}La_xS$ nO₃ exists for $x \le 0.02$ above which traces of pyrochlore La₂Sn₂O₇ were detected. These results are contrary to those of previous reports where $Sr_{0.9}La_{0.1}SnO_3$ has been reported [11]; we feel that their arguments are not entirely persuasive. Many perovskites are found to distort from the ideal cubic when the tolerance factor decreases and it has been reported that SrSnO₃ is a rotationally distorted orthorhombic body centered perovskite [12]. It is worth mentioning in our case that when quenched. SrSnO₃ crystallizes in a cubic symmetry with SG Pm3m. On the contrary, when slowly cooled it converts reversibly to an orthorhombic phase (SG Pbnm) in agreement with Ref. [13]. The ideal ASnO₃ consists of a three-dimensional lattice of regular SnO₆ octahedra sharing corners with 180° Sn-O-Sn angle and where the A-ion is basically surrounded by the nearest 12 O^{2-} . The cation displacements have found to change markedly the physical properties. The tilting of SnO₆ octahedra around the main crystallographic axis lowers the symmetry from cubic to orthorhombic phase. The lattice constants of the orthorhombic unit cell are related to that of the cubic one by $\sqrt{2}a_{\rm c} \times \sqrt{2}a_{\rm c} \times 2a_{\rm c}$. No splitting of the diffraction peaks (h00) indicating a slight distortion towards the orthorhombic structure was observed in our case. d_{exp} of $Sr_{0.98}La_{0.02}SnO_3$ (6.094 g cm⁻³) is close to that calculated on the basis of one formula weight per unit cell $(6.475 \,\mathrm{g \, cm^{-3}})$. The lattice constant of the cubic cell of doped oxide {0.40311(0) nm} increases with respect to $SrSnO_3$ {0.40191(5) nm}, revealing a very small increase in the cell size (0.8%), even though the ionic radii of La³⁺ (0.136 nm) is lower than Sr^{2+} (0.144 nm) in 12-fold coordination [14]. This is attributed to the partial reduction of $\operatorname{Sn}^{4+}(r_{\operatorname{Sn}^{4+}}=0.069 \text{ nm})$ to $\operatorname{Sn}^{2+}(r_{\operatorname{Sn}^{2+}}=0.112 \text{ nm})^1$ in octahedral site induced by La-substitution. The close lower tin ion to Sn^{4+} is Sn^{2+} that has a lone pair of electrons and does not enjoy easily octahedral coordination without deformation leading to a narrow solid solution. In insulating compounds containing Sn^{2+} , the stereo chemical pair $5s^2$ is transferred into anionic vacancies or is accommodated in a directional orbital. Sn₃O₄ exists as a well characterized discrete phase between SnO and SnO₂, where Sn(II) is located in irregular octahedral environment [16]. On the other side, when heating under reducing atmosphere, SnO is disproportionate into Sn(IV) and metallic β -Sn as checked by XRD and optical microscopy unlike TiO_2 that can be reduced to Ti_nO_{2n-1} (Magneli phase). Our attempts to reduce SrSnO₃ under diluted hydrogen flow (H₂/Ar:1/99) were unsuccessful and yielded β -Sn. The electrical measurements show that electrons introduced by La-substitution are not localized, since localization would have given rise to the formation of Sn^{2+} ions; the absence of localized Sn^{2+} in homologous oxide BaSnO₃ has been confirmed by Mossbauer resonance (manuscript in preparation).

One of the purposes of this work was to study the possibility of spin bipolaron formation. Such an electron pairing is expected to occur with post transition metals having lone pairs (groups II_A and III_A). The magnetic susceptibility χ seems an appropriate method for testing this hypothesis, i.e. verifying whether the charge carriers are normal fermions (free electrons) with spin 1/2 or spinless bosons. However, the small x-value strongly limits the validity of the method. The Mossbauer data provide a strong support for the non integral charge states and clearly show a charge disproportionation of the averaged oxidation state Bi⁴⁺ into mixed valence states in BaBiO₃ [17]. The authors found semiconductivity, no ESR signal and a small temperature- independent susceptibility resulting in mixed states $Bi^{3+/5+}$. Moreover, the structure was solved by neutron diffraction and the valence states were found to be $BaBi_{0.5}^{3+}Bi_{0.5}^{5+}O_3$ rather than $BaBi^{4+}O_3$. Bi(I) and Bi(II) are coordinated in distorted octahedral environments with different Bi-O lengths (0.228 and 0.212 nm) resulting in an ordered monoclinic perovskite [18]. The susceptibility γ of conduction electrons is given by [19]

$$\chi = (4m^* \mu_{\rm B}^2 / h^2 3^{1/3}) N_{\rm D}^{2/3} [1 - m^2 / 3m^{*2}], \qquad (1)$$

where *m* is the electron rest mass, m^* the effective mass and N_D the electron concentration. χ is positive and temperature independent (Fig. 2) with a slight slope $d\chi/dT$ of -0.005×10^{-5} emu cgs K⁻¹ in the range (75–300 K). Below 75 K, there is a sharp downturn which may be due to localized electron paramagnetic center. EPR measurements have shown that they were Fe³⁺ ions contained in the starting SnO₂. The order of magnitude of χ indicates that the oxide is intrinsically metallic but with temperature-dependent density N_D . When carriers are introduced



Fig. 2. Temperature dependence of the magnetic susceptibility χ of $Sr_{0.98}La_{0.02}SnO_{3-\delta}.$

¹The radius of cations with inert pair of electrons, such as Sn^{2+} or Sb^{3+} are not accurate and given values in the literature are somewhat variable. The radius of (Sn^{2+}) was taken from Ref. [15].



Fig. 3. Electrical conductivity vs. reciprocal temperature of $Sr_{0.98}La_{0.02}SnO_{3-\delta}$. Inset: (a) VRH plot, (b) temperature dependence of the logarithm of ρ^{-1} .

through La substitution, the susceptibility χ decreases slightly as occurs in the system $\text{Sr}_{1-x}\text{La}_x\text{PbO}_3$ [20]. An effective mass m^* (~4 m_o) was calculated from the above formula using the N_D value (= $1.04 \times 10^{21} \text{ cm}^{-3}$) deduced from the Mott–Schottky plot (see below). Such a large value is enhanced by electronic correlation expected for small polaron hopping.

3.1. Electrical measurements

As it well established, there is a strong correlation between the dopant content and the electrical conductivity in perovskite related oxides. Undoped SrSnO₃ is a white insulator; with doping of of little as 0.02 La per unit formula, it changes visibly to white grey, a color ascribed to the presence of formal Sn^{2+} ions reflecting a change in the transport properties. The electrical resistivity ρ of $Sr_{0.98}La_{0.02}SnO_{3-\delta}$ (Fig. 3) decreases with increase in temperature and clearly indicates a nondegenerate semiconducting behavior since $\rho \rightarrow a$ finite value as $T \rightarrow 0$ K with a temperature coefficient $d\rho/dT$ of $-1.26 \Omega \text{ cm K}^{-1}$. An activation energy ΔE of 40 meV was calculated of the linear portion (140–290 K) of the log ρ^{-1} vs. T^{-1} plot, hence the donors are no longer completely ionized. Similar resistivity was noted for lightly doped SrPbO₃ but the value was ~ 10 times smaller [21]. Data for fully oxidized SrSnO₃ are not presented as this oxide was found to be insulating with $\rho_{300 \text{ K}} > 10^6 \Omega \text{ cm}$. Assuming that we are dealing with a hydrogen-like donor, one expects an energy $\Delta E \propto \varepsilon^{-2}$. The dielectric constant ε is found to be 37, a value by one order of magnitude lower than that cited in the literature [22]. Formally each Sn²⁺ ion is then be present for two substituted La^{3+} and using d_{exp} , the doping rate (2%) would predict an electron concentration (N_{La}) of $2.87 \times 10^{20} \text{ cm}^{-3}$ on the basis that each La produces one electron. At the concentration $N_{\rm D}$, the average separation d between lanthanum sites and oxygen vacancies works out to be 1 nm assuming a random distribution. Hence, the expected maximum resistivity, given by $\rho_{max}(\Omega \text{ cm}) =$ $d(nm)/73^2$ [9], is 0.013 Ω cm. This value is much smaller than that observed ($\rho_{300 \text{ K}} = 30 \,\Omega \text{ cm}$) implying that the electron concentration is not determined by the chemical composition. This indicates that the itinerant electrons $N_{\rm D}$ come not only from La-substitution N_{La} but also from oxygen deficiency $(N_{\rm O})$ and the oxide is more accurately formulated Sr₉₈La_{0.02}SnO_{3- δ}. The electrons due to vacancies ($= N_{\rm D} - N_{\rm La}$) might be included in the total density and would be dominant in our case. The large ρ_{max} value is also attributed to intergrains resistive effects. The vacancies are generated during the synthesis process at high temperature under oxygen free atmosphere followed by quenching:

$$Oo \leftrightarrow \frac{1}{2}O_2 + Vo^{\bullet \bullet} + 2e^{-},$$
(2)

the species are written in accordance with Kroger–Vink notation. The strong disorder tends to reduce the mean free path l, which does not exceed one crystallographic unit and remains smaller than the length *d*. So, one can then conclude that the temperature-dependent resistivity cannot be ascribed only to a scattering mechanism. The delocalized electrons between formal states $\text{Sn}^{4+/2+}$ arise from La-donors and active oxygen vacancies whose associated electronic energy states lie in the vicinity of the bottom of CB. In-doped SrSnO₃, tin is accommodated in a mixed valent state comprising a mixture of Sn^{2+} and Sn^{4+} as required by the electroneutrality and the oxide belongs to class II in the Day and Robin classification, i.e. mixed

 $^{^2\}rho_{\rm max}.(\Omega\,{\rm cm})$ is given by the Mott relation $(hd/0.06\pi{\rm e}^2),$ h being the Planck constant.

valence compounds based on the existence of equivalent sites and activated electron transfer with polaron formation [23]. A small polaron can be expected to form when an excess of carriers move slowly so as to linger at a particular atomic position to allow the coordinate ions to adjust to its new presence. The conduction occurs through a hopping mechanism by diffusion of electrons in localized sites and involves a fixed concentration of localized electrons (n) and a concentration of available sites (N).

The electron mobility μ , defined as the averaged drift velocity in an electric field of unit strength and calculated from $\mu = (\rho N_{\rm A} e)^{-1}$, was found to be $2 \times 10^{-4} \, {\rm m}^2 \, {\rm V}^{-1} \, {\rm s}^{-1}$. Such a low μ value, compared to that of SrPbO₃ (Table 1), is attributed to the narrow antibonding CB, arising from the Sn:5s-O:2p, slightly affected by La-substitution. This can be inferred to Sn-level which is 1.4 eV lower than Pb:6s in the atomic scale [24]; Accordingly, the Pb-O bond is expected to be more covalent than Sn-O bond. This would have the effect to increase the density of states at the Fermi level in a broad CB and consequently they will a decrease of the electrical resistivity, a probable explanation of the absence of superconductivity in ASnO₃. It is interesting to notice at this level that high electron mobility can be obtained through doping with small cations which must have low electron negativity and a high nuclear charge [25].

We have pointed out the existence of a polaron contribution in homologous BaSnO₃ leading to a phonon-assisted conductivity for temperatures T exceeding $0.25\Theta_{\rm D}$ [26], $\Theta_{\rm D}$ being the Debye temperature. The activation hopping mobility is given by [27]

$$\mu = \frac{1}{6} \{ ed^2 \omega / kT \} \exp(-\Delta E_{\mu} / kT), \tag{3}$$

where ω is the attempt to escape frequency and ΔE_{μ} the energy for the self-trapped electron hopping from one site to another. For $T < \Theta_D$, ΔE_u is replaced by the point zero energy $h\omega/4\pi$ in the relation (3) and the mechanism is no longer activated. All the states become localized and $E_{\rm f}$ falls below the mobility edge E_c . Whether or not the system is insulating or metallic depends on the energy $E_{\rm f}$ which lies respectively below or above the mobility edge. Based on the Ioffe Regel criteria, Mott noticed that the metal-insulator transition occurs when the disorder extends over many lattice constant that $k_{\rm f} l < 1$ [10], where $k_{\rm f}$ is the wave vector. In metallic regime, $k_{\rm f}l$ has the same order of magnitude as the interatomic distances. The introduction of imperfections with different nature (phonon, impurities, etc.) in the crystal lattice perturbs the electrons propagation and leads to a nonuniform phase variation. Anderson outlined that

Table 1 Relative energies and related physical properties of SrBO₃

in a random potential, the electrons wave function becomes localized if the quantity (V_o/B) is larger than a critical value $(V_o/B)_{crit}$, V_o is the fluctuation potential and B the band width. A value of 1.5 is generally adopted in six-fold coordination [9]. The electrons are described by a wave function whose amplitude decreases exponentially with the distance r ($\psi(r) = e^{-r/\xi}$ with, ξ the localization length). Mott noticed that the defect states at energy level within the forbidden band (band tailing) are more susceptible to localization. When the electrons are localized with a finite density of states, energy dispersion occurs at the level $E_{f.}$

Attempts to fit the electric data to a linear law over the whole temperature range were not successful (inset b, Fig. 3). The metal-insulating transition seems to of Anderson type resulting from the chemical disorder of donors as well as oxygen vacancies where a departure from the potential periodicity results with a residual independent resistivity at low temperatures. In the range (9–20 K), the mechanism conduction changes to VRH (inset a, Fig. 3), the exp $\left[-(T_{0}/T_{0})\right]$ T)^{1/4}] behavior of the resistivity extends over many crystallographic units than nearest neighbors. In such a case, the thermo-power S is predicted to have a temperature dependence $S \propto T^{0.5}$ when the density of states is an energy independent function (inset a, Fig. 4). In addition to Anderson localization, a local charge electron produces a distortion particularly in ionic oxides which built an energetic electron trap. The grain boundaries in polycrystalline oxides form potential barriers against electron hopping but have only a small influence on the thermopower S. The small heat conductivity of SrSnO₃ at low conductivity made it possible to use large gradient temperatures and hence to continue the measurement down to liquid helium temperature. In the case of a metallic conductivity, S is given by [9]

$$S = (\pi^2 k^2 T/3e)(\partial \ln \sigma(E)/\partial E)_{E=E_\ell},$$
(4)

with an accuracy of the order of $(kT/E_f)^2$, $\sigma(E)$ is the conductivity the oxide would have if E_f is equal to E, i.e. at the Fermi surface. S is negative, confirming that the dominant carriers are electrons. At rising temperature, the thermal excitation of impurities which lie below CB occurs progressively and S can be expressed as

$$S = -k/e(\Delta E/kT + A) = (k/e)\ln(n/N),$$
(5)

where A is the dimensionless kinetic term proportional to average electron energy not easy to evaluate and can be neglected for $E_g \ge 4 kT$. The linear increase of |S| with T (Fig. 4) indicates electron mobility μ thermally activated. ΔE is large compared to thermal energy kT (26 meV); hence

SrBO ₃	Color	$E_{\rm ion}$. (eV) ^a	$-E_{\rm ns}~({\rm eV})^{\rm a}$	$\mu_{300\mathrm{K}}~(\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1})$	$E_{\rm g}~({\rm eV})$	$\rho_{300\mathrm{K}}~(\Omega\mathrm{cm})$	<i>m</i> * (<i>m</i> _o)
SrSnO ₃	White	Sn: 7.34381	5s: -10.77	10^{-4} ~0.1	4.32	30	4
SrPbO ₃	Black	Pb: 7.41666	6s: -12.19		1.78	2.5	1.5

^aTaken from Ref. [24].



Fig. 4. Temperature dependence of the thermo-power S for $Sr_{0.98}La_{0.02}SnO_{3-\delta}$. Inset: (a) the thermo-power S plotted as a function of $T^{0.5}$, (b) data of S at high temperatures.

most of electrons are localized in shallows donors and follow a Boltzmann statistic. So we are in a case where both the mobility μ and the concentration N_D are thermally activated. In addition, because of the phonon–electron interaction, the electrons move by a phonon-assisted hopping over localized Sn^{2+} and this gives rise to a mass enhancement. The slight deviation of S(T) from the linear behavior at low temperatures accounts for the phonon drag effect which can take place. On the contrary, above 660 K, S becomes temperature independent (inset b, Fig. 4); such a behavior is typical of a small polaron hopping involving a temperature-independent carrier density. This value can be assimilated to equilibrium temperature of reaction (2), above which the fully oxidized perovskite is restored and indicates reversible oxygen extraction/insertion.

3.2. Optical absorption and photo electrochemistry

The irradiation of SC by a photon with energy hv greater than the optical gap $E_{\rm g}$ promotes an electron from VB to CB. The separation of the photogenerated electron/hole (e^{-}/h^{+}) can be achieved through the electric field that takes place spontaneously in the depletion width W of SC. When n-type SC is brought into contact with an aqueous solution, an equilibrium is established with equalization of SC Fermi level and the electrochemical potential of the solution results in upward band bending $\Delta U (= E_f - E_{red})$ of the electronic bands near the interface. The maximal photovoltage ($\sim E_g/e$) is governed by ΔU and at equilibrium it is imposed by the redox potential of $M^{2+/0}$ and the flat band potential ($V_{\rm fb}$) of SC. In order to get a high ΔU value, i.e. an efficient separation of the pairs (e^{-}/h^{+}) , E_{f} must be low and this restriction supposes the SC electron affinity to be as small as possible. Optical data combined

with the PEC characterization lead to the determination of energy band diagram. The variation of the transmittance of SrSnO₃ in the range 200–800 nm (Fig. 5) exhibits a sharp onset corresponding to the absorption edge. When the ratedetermining step in the PEC process is the arrival of electrons at the interface, the quantum efficiency η is given by [28]

$$\eta = J_{\rm ph}/\Phi = 1 - \exp\{-\alpha W\}\{1 + \alpha L_{\rm p}\}^{-1},\tag{6}$$

where Φ is the light flux, $L_{\rm p}$ the diffusion length, and the width W is given by $(\varepsilon\varepsilon_{\rm o}\Delta U/2\pi e^2 N_{\rm D})^{0.5}$. η is proportional to the optical absorption coefficient α if both the lengths W and $L_{\rm p}$ are less than the penetration depth α^{-1} ($\alpha L_{\rm p}$ and $\alpha W \ll 1$). These conditions are met in our doped oxide and in such a case, α varies as

$$(\alpha hv)^n = A(hv - E_g). \tag{7}$$

The plots of $(\alpha hv)^n$ vs. hv should be linear and permit the determination of inter band transitions energies. The exponent *n* equals 0.5 and 2, respectively, for indirect and direct allowed optical transitions. The intercept with the *hv*-axis yields a gap E_g of 4.32 eV (inset a, Fig. 5), a value very close to that determined elsewhere (4.27 eV) [29]. Further indirect transition occurs at 4.04 eV (inset b, Fig. 5).

SrSnO₃ was found to have an excellent chemical inertness over the whole pH range. The J(V) characteristics of Sr_{0.98}La_{0.02}SnO_{3- δ} in KOH (1 M) plotted both in the dark and under illumination are represented in Fig. 6. The dark current J_d is small over a large potential range showing a good electrochemical stability. The significant amount of J_d at potential more cathodic than ~ -1.20 V is due to H₂-evolution (gas bubbles are noticeable on the electrode). In the dark, two distinct waves of similar



Fig. 5. Reflectance diffuse spectrum of $Sr_{0.98}La_{0.02}SnO_{3-\delta}$. Inset: (a) determination of the direct band gap (n = 2), (b) indirect band gap (n = 0.5).



Fig. 6. The J(V) characteristics of $Sr_{0.98}La_{0.02}SnO_{3-\delta}$ both in the dark (----) and under illumination (- - -). Inset: (a) cyclic plot in the dark, (b) relationship of J_{ph}^2 vs. potential.

surfaces are easily seen on the cyclic curve J(V) (inset a, Fig. 6). It is our opinion that this behavior makes it possible to conclude that the electrochemical peaks located at -0.41 (O₁) and -0.14 V (O₂) are ascribed to the oxidation of Sn²⁺ according to

$$SrSnO_{3-\delta} + 2\delta OH^- \rightarrow SrSnO_3 + \delta H_2O + 2\delta e^-.$$
 (8)

This indicates that Sn^{2+} comes from La-substitution and oxygen extraction and both kinds are nonequivalent implying that the crystallographic sites of Sn^{2+} are different. So, one can anticipate that Sn^{2+} originating

from oxygen departure becomes less coordinate and easy to oxidize (peak O₁) because of the lower potential barrier for the electron hopping than that coming from La-substitution (peak O₂). Both oxidations occur at potentials preceding the oxygen evolution avoiding a mixed process and quantifying accurately the δ -value. Finally the transition to region (*M*) is accompanied by the O₂-bubbling. During the reverse cathodic scan, the two peaks located at -0.57 (R_2) and -0.83 V (R_1) correspond respectively to reductions of O₂ and O₁. It is helpful to outline that the ratio of the peaks areas (O₁/O₂ = \sim 4) is close to that of the electron concentrations ($N_O/N_{La} = \sim 2.7$) calculated above lending further support is the above hypothesis. In addition, the existence electrochemical peaks corroborate the weak delocalization of the inert pair 5s² and the less metallic behavior compared to homologous BaSnO₃ (manuscript in preparation).

Upon scanning the potential towards the anodic direction potential while n-type SC is irradiated, there will be a potential $V_{\rm on}$ at which the photocurrent $J_{\rm ph}$ just appears $(J_{\rm ph} = 0 \text{ when } V = V_{\rm fb})$.

$$J_{\rm ph} \propto (V - V_{\rm fb})^{0.5},$$
 (9)

where the anodic $J_{\rm ph}$ is an intrinsic property attributed to PEC behavior. The shape of the $J_{ph}(V)$ curve and the positive direction of J_{ph} provide unambiguous evidence of n-type semiconductivity confirming the negative values of the thermo-power. At pH 13.6 (KOH 1 M), the $J_{\rm ph}(V)$ curve gives an onset potential of -0.46 V. It is also seen that $J_{\rm ph}$ increases and reaches a saturated value at ~ -0.35 V, a behavior ascribed to a zero recombination process of (e^{-}/h^{+}) pairs at grain boundaries. The onset potential (V_{on}) , at which J_{ph} starts to flow, outlines the position of the conduction band. If no (e^{-}/h^{+}) pairs recombination would occur, Von can be reasonably assimilated to the potential $V_{\rm fb}$. Generally, the difference " $V_{\rm fb} - V_{\rm on}$ " decreases with increase in the incident light. On a more quantitative way, it is known that for perovskite oxides $V_{\rm fb}$ usually changes by $-0.059 \,\mathrm{V/pH}$. As expected, $Sr_{.98}La_{0.02}SnO_{3-\delta}$ exhibits a pH-dependent potential V_{fb} and the band edges were observed to shift by $55 \pm 5 \text{ mV}$ per pH unit in the range (7–14). The relationship between J_{ph} and the potential is expressed by

$$J_{\rm ph}^2 = \cos \alpha^2 W^2 (V - V_{\rm fb}), \tag{10}$$

a $V_{\rm fb}$ value of -0.49 V was deduced by extrapolating the curve to $J_{\rm ph}^2 = 0$ (insert b Fig. 6). However, the accurate $V_{\rm fb}$ value was determined independently from the impedance spectroscopy according to the Mott–Schottky formula (neglecting the roughness factor):

$$C_{\rm s}^{-2} = (0.5\varepsilon\varepsilon_{\rm o}qn)^{-1} \{ V - V_{\rm fb} - kT/q \},\tag{11}$$

where $C_{\rm s}$ is the space charge capacitance and the other constants have their usual meanings. $V_{\rm fb}$ and $N_{\rm D}$ were calculated respectively by extrapolating the curve C^{-2} vs. the V-axis and from the slope $(0.5eN\varepsilon_{\rm o})^{-1}$ of the linear plot (Fig. 7). $N_{\rm D}$ was found to be 1.04×10^{21} cm⁻³ whereas the voltage axis intercept gives a potential $V_{\rm fb}$ of +0.01 V at pH 7. The $V_{\rm fb}$ value extrapolated to pH 13.6 (KOH 1 M) on the assumption that $V_{\rm fb}$ changes at the ratio of -0.055 V pH⁻¹ is -0.34, in agreement with that found from the $J_{\rm ph}(V)$ characteristics (-0.48 V).

The II–VI perovskites ABO₃ show a more ionic character particularly with alkaline earth rare elements A (group II_A) having wide forbidden band E_g . Higher the ionic character of the A–O bond and larger the covalency of B–O bond, stronger the effect of broadening CB of B ns character. The Sn:5s is about 1.4 eV lower than Pb:6s [24].



Fig. 7. Mott–Schottky plot for $Sr_{0.98}La_{0.02}SnO_{3-\delta}$ in KCl 1 M.

Accordingly the Sn–O bond is expected to be more ionic than the Pb–O bond and this should decrease the density of states at the level $E_{\rm f}$. The difference between Sn:5s and O:5p orbitals accounts for the smaller overlap in SrSnO₃ leading to a narrow CB width, a larger optical gap and a lower mobility (Table 1). On the contrary, in SrPbO₃, the electrons travel in the wide s– $p\sigma^*$ antibonding CB due to the closeness in energy of Pb:6s and O:2p and hence to stronger covalency. This conclusion is also corroborated by the smaller resistivity and the lighter mass m^* for SrPbO₃.

For practical applications, the potential $V_{\rm fb}$ is not negative enough for n-type specimen owing to the large electron affinity of tin: This should give rise to a low band bending ΔU at the SC/electrolyte interface and a high recombination rate of (e^{-}/h^{+}) pairs. In addition, the free potential $U_{\rm f}$ of n-SrSnO₃ is negative of the potential $V_{\rm fb}$ and this implies that the photoreactions do not occur without external assistance bias. On the other hand, the known susceptibility of most narrow band gap SCs to photocorrosion requires a protective layer. One strategy to overcome this handicap and preclude electrolyte attack consists to deposit a transparent oxide layer. Doped SrSnO₃ is an eventual candidate for coating materials that satisfies the following criteria: (1) a high light passing in the whole solar spectrum, (2) an appreciable electronic conductivity, (3) a long-term chemical stability over a large pH range.

4. Conclusion

The physical properties of $SrSnO_3$ are significantly changed when doped with La^{3+} onto the Sr-sublattice. The solid solution $Sr_{1-x}La_xSnO_3$ had a very narrow domain and turned to biphasic system for x > 0.02 where the limit composition coexists with the pyrochlore La_2S n_2O_7 , a behavior attributed to the inert electronic pair 5s². An effective mass of 4 m_0 was deduced from the magnetic susceptibility. The electron concentration, assuming that each La gives one electron to the conduction band, is lower than that calculated from the maximum resistivity ρ_{\min}^{-1} and this indicates that itinerant electrons assimilated to Sn^{2+} comes equally from oxygen deficiency. The conduction occurs by low polaron hopping of electrons between localized ions $\operatorname{Sn}^{4+/2+}$ where both the electron mobility and the doping density are thermally activated. At low temperatures, the conductivity mechanism changes to a variable range hopping. From optical measurements, it was found that the band gap is 4.42 eV and the transition is directly allowed. The photoelectrochemical characterization confirms the n-type semiconductivity. The flat band potential measured from capacitance measurements was very close to the onset of photocurrent. The energy difference between Sn:5s and Pb:6s orbitals accounts for the weak overlap with $O^{2-}:2p$ orbital leading to a narrow band width and a larger optical gap in SrSnO₃.

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