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OXYGEN STOICHIOMETRY, CONDUCTIVITY and GAS SENSOR PROPERTIES of BaSnO$_3$

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Abstract

BaSnO$_3$ powder loses a small amount of oxygen in air at high temperatures leading to significant changes in its electronic conductivity. At 1300 °C, it has the stoichiometry BaSnO$_{2.9999}$. The oxygen deficiency can be preserved by quenching to room temperature but the oxygen loss is reversible and reoxidation commences above about 300 °C. The n-type conductivity of quenched material at 300 °C, $1 \times 10^{-5}$ ohm$^{-1}$cm$^{-1}$, is four orders of magnitude higher than that of the same fully oxidised, slow-cooled material. Oxygen-deficient BaSnO$_3$ shows rapid sensitivity to an increase in oxygen partial pressure; it is also sensitive to moisture and then shows proton conductivity.

Introduction

BaSnO$_3$ exhibits a range of properties when pure or doped that lead to a variety of possible applications. In its pure state, it has the perovskite structure and is insulating with a band gap of around 3.5 eV [1-4]; possible applications as a capacitor dielectric have been proposed [5]. When prepared under reducing conditions, it is oxygen-deficient, metallic and has a high electron mobility [6,7], leading to possible transparent conductor [8] and solar cell [9] applications. Numerous studies have reported the use of BaSnO$_3$ as a sensor to a range of gases [10-15], including humidity [1,16-18].

Usually, BaSnO$_3$ is regarded as a modest n-type semiconductor [10,15,19-20], possibly associated with a small oxygen deficiency, but in other reports it is given as p-type [12]. Only one attempt to quantify the oxygen deficiency has been reported [7,21,27] with a value for $\delta$ in the formula BaSnO$_{3-\delta}$ of 0.027 for a sample prepared by pulsed laser deposition, PLD, in a low oxygen partial pressure, pO$_2$ atmosphere, 0.3 Pa.

BaSnO$_3$ has been prepared by various routes, including high temperature solid state reaction of oxide mixtures [6,24], sol-gel methods [22,25] and hydrothermal synthesis [15,23,26]. Films have been prepared by PLD [7]. Oxygen-deficient samples have also been
prepared by heating in evacuated silica ampoules [6,21,27], sometimes with the addition of Fe as an oxygen getter.

The purpose of this work was to quantify the possible oxygen non-stoichiometry of BaSnO$_3$ at high temperatures, correlate this with the electrical properties and understand the inter-relationships between processing conditions, oxygen stoichiometry, electrical conductivity and sensor action. Numerous reports in the literature consider the factors and conditions that influence sensor action, but the role of oxygen non-stoichiometry is not well-established. A key experimental technique in this work has been to quench samples to room temperature after equilibration at a range of high temperatures, thereby preserving the high temperature state and allowing it to be studied at lower temperatures, with or without subsequent oxidation to recover its original equilibrium oxygen content. This experimental strategy is vital because samples that lose oxygen during heating at high temperatures may undergo varying degrees of reoxidation during cooling, depending on the cooling rate; the cooling step is therefore a variable in materials processing that needs to be controlled and/or understood because it can have a major influence on the subsequent properties.

**Experimental**

BaSnO$_3$ powder was prepared by solid state reaction. BaCO$_3$ and SnO$_2$ powders of high purity (99.9%) were weighed to give the stoichiometric formula BaSnO$_3$. The powder was mixed and milled manually in acetone using a mortar and pestle for 30 min, pressed into pellets and placed on sacrificial powder of the same composition on Pt foil. Initial firing was at 1000 °C for 6 h to eliminate CO$_2$, after which the pellets were ground, repressed, fired at 1250 °C for 8 h in air, and then cooled slowly by switching off the furnace.

Phase analysis was carried out by X-ray powder diffraction, XRD using a Siemens D5000 diffractometer. Samples of a few mg were placed in a circular holder and inserted in the rotating stage of the diffractometer. Data were collected over 20° ≤ 2θ ≤ 70° using monochromated Cu Kα$_1$ radiation, λ =1.5406Å with step size 0.02° at 1°/min. Collected data were processed using the WinXPOW software package {version 1.06, stoe and Cie GmbH, Darmstadt}. The reaction product was shown to be phase-pure BaSnO$_3$, Fig.1.

To prepare sintered pellets for impedance measurements, BaSnO$_3$ was pressed into pellets of either 8 or 20 mm diameter at 0.6 tonnes, placed on sacrificial BaSnO$_3$ powder in a
Pt crucible and fired at 1300 °C for 8 h in air. Typical pellet densities were 55–62% with a porous microstructure consisting of interconnected grains of size ~0.5–2.5 mm, Fig. 2. The sintered pellets were given subsequent heat treatments and either quenched to room temperature after heating at 1000 to 1300 °C in air for 2 h, or slow-cooled in O₂ to room temperature after heating at 900 °C in O₂ for 2 h. Pt paste was brushed onto opposite pellet surfaces which was dried and hardened at 900 °C for 1 h to form electrodes.

To collect impedance spectroscopy, IS, data, pellets with electrodes attached were connected to the Pt wires of a conductivity jig which was placed in a horizontal tube furnace, through which different gases could be passed, Fig. 3. Before each measurement, the jig and sample was allowed to equilibrate, typically for 10–30 min and then IS data recorded. Dry and wet atmospheres were obtained by passing the desired gas through Dreschel bottles containing either silica gel or water before entering the conductivity jig. IS data were collected isothermally at temperatures between 180 and 700 °C using a Hewlett Packard 4192A (HP) over the frequency range 1 Hz to 1 MHz. In all cases, the nominal applied voltage was 100 mV; data were corrected for the geometric factor of the sample and for the blank impedance of the cell (i.e. short circuit resistance of the leads and open circuit capacitance of the sample holder and jig). IS data were modelled with various equivalent electrical circuits using ZView software.

Gas sensor studies used the same samples, experimental set-up and instrumentation that was used for IS. Thus, porous pellets of typical dimensions 8 mm diameter and 1 mm thickness were used with electrodes made from dried and hardened Pt paste. Gas flow rates were controlled by passing gases through a bubbler placed before and / or after the sample set-up, as appropriate, with a typical flow rate of 1-3 bubbles sec⁻¹. The humidity of wet atmospheres was not measured directly but was taken to be the water vapour pressure associated with the water bubbler at different temperatures, e.g. 7.4 kPa at 40 °C.

Results
In order to determine whether BaSnO₃ loses oxygen at high temperature, a series of experiments was performed in which a sample of ~3 g was given a second heating at 900 °C in O₂ for 2 h, slow-cooled to room temperature, heated isothermally at different temperatures, quenched and weighed. The sample weight was determined on stepwise heating over the range 25 to 1500 °C followed by stepwise cooling, Fig. 4. The value of the oxygen content, 3-δ, was calculated as a function of temperature and is shown using the right ordinate scale of
Fig 4; to calibrate the scale, it was assumed, as a point of reference, that the sample cooled stepwise to room temperature was oxygen-stoichiometric BaSnO$_3$.

During first heating, weight loss commenced above ~400 °C and continued up to the highest temperature, 1500 °C. On cooling, the weight lost above ~800 °C was regained but not the weight lost at lower temperature. Fully reversible data were then obtained during cooling and second heating over the range 25-1500 °C and are attributed to gain / loss of O$_2$. The oxygen content appeared to be constant below ~ 200 °C and decreased increasingly rapidly at higher temperature. At 1500 °C, the oxygen content corresponded to the formula BaSnO$_{2.99983}$. During first heating, the sample showed an additional weight loss over the range ~ 400-800 °C which was not regained on cooling; this is attributed to loss of water.

A selection of typical impedance data at several temperatures is shown in Fig. 5. The impedance, $Z^*$, complex plane plots, (a), showed a single arc whose low frequency intercept on the $Z'$ axis gave the total resistance of the sample, $R_T$. Log $Y'$ vs log f plots, (b), showed at lower frequencies a plateau corresponding to the total conductivity, $R_T^{-1}$ and a power law dispersion at higher frequencies. The same data replotted as log $C'$ vs log f, (c), showed one plateau at higher frequencies with value ~5.1 pF and a dispersion at low frequencies. The value of 5.1 pF cm$^{-1}$ for the high frequency plateau corresponds to the sample bulk which has a limiting high frequency permittivity, $\varepsilon'_\infty$, of value ~ 58, given by

$$\varepsilon'_\infty = C / e_o$$

where $e_o$ is the permittivity of free space. 8.854 Fcm$^{-1}$.

Impedance, $Z''$ and modulus, $M''$ spectra of the same data, Fig. 5(d), show in each case a single peak with their maxima at similar frequency. The full width half maximum, FWHM, of the $M''$ peak, 1.65 decades, is somewhat greater than that expected for an ideal Debye peak, 1.14 decades. This indicates that an appropriate equivalent circuit to represent the experimental data is a parallel resistance-capacitance, RC element modified by the inclusion of a constant phase element, CPE to account for the dispersion in $Y'$ and $C'$, as shown in fig 6(a) inset; this equivalent circuit is frequently used to model the bulk electrical properties of ionic and electronic semiconductors. The CPE is, effectively, a parallel combination of a frequency-dependent resistor and capacitor; the relative contribution of each to the overall, frequency-dependent admittance is governed by the power law exponent, $n$. It takes the form

$$Y^* = A\omega^n + jB\omega^n$$

where $j = \sqrt{-1}$ and $B/A = \tan (n\pi/2)$.
Fitting of impedance data to this circuit is shown in Fig. 6 for one dataset for a sample quenched from 1000 °C and measured at 175 °C. Excellent fitting results were obtained, as shown at 175 °C and over the temperature range 175 to 300 °C. The temperature dependence of the fitted parameters is summarised in Table 1. We conclude, therefore, that the measured impedance data are dominated by the bulk response of the sample with no significant contribution from either grain boundary or sample-electrode contacts.

Bulk conductivity data, \( \sigma_b \), for a range of samples are shown in Fig. 7. Slow-cooled samples were measured in O\(_2\) to avoid possible O\(_2\) loss during the impedance measurements. By contrast, quenched samples were measured in N\(_2\) to avoid the possibility of oxidation during IS measurement. The data show that, depending on annealing temperature and cooling rate, conductivities varied greatly between two extremes of behaviour, first, for a sample quenched from 1300 °C and second, for a sample slow-cooled in O\(_2\). Between these two extremes, samples quenched from lower temperature showed intermediate conductivities. The results shown in Fig 7 were fully reversible on heat-cool measurement cycles over the range 180 to 300 °C. The difference in conductivity between the two extremes was, by interpolation, about four orders of magnitude at 500 °C; activation energies ranged from 0.88 to 1.11 eV. These data are fully consistent with n-type conduction that is controlled by the degree of oxygen nonstoichiometry, \( \delta \), shown in Fig. 4. Thus, electrons are liberated as oxygen is lost from the sample by:

\[
2\text{O}^{2-} \rightarrow \text{O}_2 + 4e \quad (3)
\]

Large changes in conductivity occur for very small changes in \( \delta \), Figs. 7 and 4.

The quenched samples, which are oxygen-deficient, are in a metastable state but are kinetically stable over the range 180 to 300 °C and do not reoxidise during the impedance measurements. However, reoxidation of quenched samples commenced at temperatures above ~300 °C, as shown by a time-dependent increase in resistance at constant temperature, shown in Fig. 8 for the sample quenched from 1000 °C and measured after different times at 325 °C. From these resistance changes and comparison with the conductivities of quenched and slow-cooled samples shown in Fig. 7, the data in Fig. 8 show that oxidation of the sample bulk had commenced but the process was incomplete, even after 40 mins at 325 °C.

A conductivity Arrhenius plot is shown in Fig. 9 over the range 180-700 °C for a sample quenched from 1000 °C. On first heating, data are approximately linear to ~300 °C, but the resistance increased at higher temperature before decreasing again above ~500 °C.
Reversibility in conductivity was then seen at higher temperatures and in subsequent cool-
heat cycles. The data in Fig. 9 show three regions: (i) below ~300 °C associated with a
metastable, oxygen-deficient state of the quenched sample; (ii) between 325 and 450 °C
associated with sample oxidation, even in a N₂ atmosphere during the impedance
measurements; (iii) above 500 °C, with fully reversible temperature dependence associated
with equilibrium behaviour.

The sensitivity of BaSnO₃ to pO₂ at two temperatures, 300 and 500 °C, was
investigated by switching between dry O₂ and dry N₂ during IS measurements; data are
shown in Fig. 10. The tests commenced with a fully oxidised sample of BaSnO₃. On
switching from O₂ to N₂, conductivity increased by 1 to 1.5 decades to reach a steady state in
10 mins at 500 °C. A similar increase occurred at 300 °C but needed ~200 minutes to reach a
steady state. On switching back to O₂, the conductivity decreased rapidly to its initial value,
even at 300 °C. This rapid decrease in a short time indicates the potential usefulness of
BaSnO₃ as a sensor to an increase of pO₂. As a possible sensor to reduction in pO₂, the
change in conductivity on switching from O₂ to N₂ is more slow, however, especially at 300
°C.

A more complete survey of the sensitivity[29] to pO₂ over the temperature range 200
to 700 °C is given in Fig 11. The sample used for this experiment was quenched from 1000
°C. Starting at 200 °C, the conductivity was measured first in N₂, second in O₂ and third in N₂
again. For the final measurement in N₂, sufficient time was allowed for the conductivity to
reach a steady state. The same sample was then reheated at 1000 °C for 30 mins to recover
its equilibrium state at that temperature, quenched and IS measurements in the N₂, O₂, N₂
sequence repeated at the next temperature. Data were obtained in this way at temperatures
between 200 and 700 °C, as shown in Fig. 11.

The quenched sample showed high sensitivity to pO₂ up to ~ 300 °C: on changing
from N₂ (data points 1) to O₂ (data points 2), its resistance increased rapidly by three orders of
magnitude, although the time-dependent response profile was not measured accurately. On
remeasuring in N₂ (data points 3) the conductivity increased but did not regain the original
value even though a steady state was reached.

At intermediate temperatures, ~300-500 °C, sample oxidation occurred, even in N₂
(data points 1). At the highest temperature, ~500 °C, conductivity was reversible on
switching between N₂ and O₂; data represent the equilibrium response of the sample to pO₂.
There is some indication from weight change studies, Fig. 4, that oxygen-deficient BaSnO$_3$ may pick up water on cooling. This is further shown by IS measurements of quenched BaSnO$_3$ in dry and wet N$_2$, Fig.12(a): the total conductivity at 200 °C was three times greater in wet N$_2$ than in dry N$_2$. Conductivity Arrhenius plots are shown in Fig.12(b) on samples quenched from 1300 and 1000 °C and measured in both dry and wet N$_2$ (DN and WN) over the temperature range ~150-300 °C. In both cases, the conductivity is higher and the activation energy lower in wet N$_2$.

The effect of water vapour partial pressure, pH$_2$O and the reversibility of conductivity changes to both pH$_2$O and pO$_2$ is shown in Fig.13(a). IS data were measured at 700 °C on a sample of BaSnO$_3$ quenched from 1000 °C. The first measurements were in O$_2$, followed by N$_2$. The effect of pH$_2$O was then shown by bubbling N$_2$ through a water bath at temperatures in the range 0 to 40 °C. The changes seen were fully reversible and may be interpreted as follows: in a dry atmosphere, conduction was electronic and therefore, increased with a decrease in pO$_2$; in a wet atmosphere, the conductivity increased with increasing pH$_2$O and became primarily protonic. Proton conductivity depends on the ability of BaSnO$_3$ to absorb H$_2$O and this appears to require oxygen vacancies, as shown by the higher conductivity in samples quenched from 1300 °C compared to those quenched from 1000 °C, and measured in wet N$_2$, Fig.12(b):

$$\text{H}_2\text{O(gas) + V}_{\text{O}}^{\cdot\cdot} + \text{O}^{\cdot\cdot}_{\text{O}} \rightarrow 2\text{OH}^{\cdot}$$  \hspace{1cm} (4)

This is further shown by data in Fig.13(b), recorded at 550 °C in atmospheres of dry and wet O$_2$, N$_2$ and CO$_2$. Commencing with dry O$_2$, there is only a small, reversible increase in conductivity in wet O$_2$. A large increase in conductivity occurs, and to a similar extent, in both dry N$_2$ and CO$_2$ due to electrons released by O$_2$ loss. The conductivity subsequently increases further in wet atmospheres due to pick-up of H$_2$O by the oxygen vacancies that have been created.

Further evidence that conduction in a wet atmosphere is principally ionic rather than electronic is shown by low frequency IS data recorded at room temperature and for frequencies down to 10 mHz in Fig. 14. In addition to the impedance arc that represents the bulk response of the sample, a low frequency ‘spike’ is seen characteristic of a blocking capacitance at the sample-electrode interface. At the lowest frequencies, the C' data increase to ~60 µFcm$^{-1}$, consistent with a double layer capacitance and therefore, ionic (protonic) conduction through the sample bulk.
Discussion

The weight change results, Fig. 4, show that BaSnO$_3$ is slightly oxygen-deficient at high temperatures. Above ~500 °C, it loses and regains oxygen reversibly on changing either the temperature or pO$_2$. Its formula may be written as BaSnO$_{3-x}$ with a value for $\delta$ of for instance, 0.0001 at 1300 °C in air. This is based on the assumption that the sample subjected to stepwise slow cool from 1500 °C was fully oxygen-stoichiometric at room temperature, Fig. 4. The oxygen deficiency at high temperatures can be preserved to room temperature by quenching (rapid cool of small samples in air, by removing from the furnace, or by dropping into liquid N$_2$). The resulting samples are metastable but commence oxidation on heating, at a rate that depends on temperature, time and pO$_2$.

No previous studies on the possible oxygen non-stoichiometry of BaSnO$_3$, prepared by solid state reaction and heating in air, have been reported. Perhaps this is because the variations in oxygen content are small, occur under equilibrium conditions at high temperatures and are likely to be detected only in rapidly-cooled samples since various amounts of re-oxidation and/or water pick-up occur during cooling, depending on cooling rate. As far as we are aware, the only other estimate of oxygen deficiency, $\delta$, is for a sample grown as a film by pulse laser deposition, PLD, at 0.3 Pa of oxygen pressure, with a value $\delta = 0.027$ [7]. Although small, this is significantly higher than the values reported here and is attributed to the much more reducing conditions in the PLD chamber. These film samples have much higher electronic conductivity than the ceramic samples studied here, which is further evidence for their increased oxygen deficiency.

The variation in $\delta$ with sample processing conditions is very small and at the limits of what can be detected easily by weight change measurements on small samples. In addition, weight measurements give an overall sample weight and for instance, are unable to discriminate between surface and bulk oxidation. The electrical properties are, however, very sensitive to the weight changes since, as shown by eq’n (3), oxygen loss is associated with ionisation of oxide ions and the electrons that are liberated lead to a dramatic increase in electronic conductivity. For this reason, we are able to determine from impedance measurements that samples lose and gain oxygen at temperatures as low as 200 °C although, as shown in Fig.11, the oxygen that is gained on switching the atmosphere from N$_2$ to O$_2$ is not fully lost on switching back to N$_2$. It is, therefore, highly likely that the reactions associated with oxygen loss/gain are surface-controlled and are rapid, but diffusion of oxide
ions into/out of the sample interior is a much slower process and limited to higher temperatures. This is consistent with the observation [14] that ‘BaSnO$_3$ seems to be an example material for both the reactions of the gas atmosphere with the grain bulk at high temperatures and reactions at the grain surface at lower temperatures.’

A consequence of the temperature-dependent rate of oxidation of oxygen-deficient samples on cooling is that oxygen concentration gradients are likely to develop in samples that were initially homogeneous and oxygen-deficient but subsequently, had oxidised partially. It is also possible that samples prepared in different laboratories and/or under different experimental conditions may either have different degrees of oxygen non-stoichiometry or be inhomogeneous in their oxygen content, but this may remain undetected since there is no easy method to analyse small oxygen concentration gradients at sample surfaces.

A number of reports have used IS to measure electrical properties, with the general observation that either one or two impedance components are detected and attributed to grain and grain boundary contributions [14, 25]. It is stated [22] to be ‘widely-accepted that Schottky barriers between particles govern the electrical properties’. This implies the presence of a dominant, low-frequency, voltage-sensitive contribution to the impedance data, which is not observed with our data. Voltage-sensitive Schottky barriers are also not expected in measurements using electrode contacts that are fabricated to be ohmic [24]. There are, therefore, doubts as to the validity of the proposed, Schottky barrier-related mechanism of sensor action.

The above considerations point to the importance of surface reactions in determining the sensitivity of sample conductivity to pO$_2$. Nevertheless, as far as we can tell, the changes in electrical conductivity are not limited to surface conductivity but are associated with the sample bulk, ie sample grains. Thus, most samples are electrically homogeneous with no evidence of, for instance, either resistive grain boundaries or conductive grain cores. Impedance data for our ceramic samples are modelled well by the equivalent circuit, Fig.6(a) inset, which is essentially a single parallel RC element that also includes a CPE to account for non-ideal departures from a Debye-like response. The implication, therefore, is that the sample bulk conductivity responds to oxygen exchange reactions that occur at the sample surface. This is an important conclusion for understanding the sensor response mechanism in materials such as porous ceramics of BaSnO$_3$. 
We find no evidence from the impedance data for Schottky barriers at either sample-electrode or interparticle interfaces. Schottky barriers form spontaneously at interfaces and are associated with electron transfer across the interfaces. They are detected as additional impedances in the equivalent circuit that represents the sample response and are generally, thin layer, high capacitance effects that are detected at the lower frequency end of the overall impedance spectrum. Since Schottky barriers are voltage barriers rather than material barriers, they are sensitive to an applied voltage, which provides a method to discriminate between impedances that are sample-related and Schottky barrier-related. We see no evidence of voltage-sensitive impedances in our BaSnO$_3$ data, but further studies to confirm this would be worthwhile.

The possibility of H$_2$O involvement in the electrical properties of BaSnO$_3$ has been investigated, either as a source of proton conduction [25,28] or as a mechanism of enhanced CO$_2$ sensitivity through surface carbonate formation [12]. Samples that are oxygen-deficient are sensitive to moisture, which is adsorbed, ideally, by mechanism (4). Samples that are fully oxidised, at least at their surfaces, show little sensitivity to moisture, Fig.13(b), whereas oxygen-deficient samples are sensitive to moisture in atmospheres of either N$_2$ or CO$_2$. The impedance response also depends on pH$_2$O (a). The changes are rapidly reversible on switching between dry and wet atmospheres. The increase in conductivity in wet atmospheres is attributed to proton conduction; good evidence for this is obtained from low frequency impedance data, Fig.14, showing the appearance of an additional impedance effect associated with a blocking capacitance that, from the magnitude of the capacitance, is associated with the sample-electrode interface.

Oxygen-deficient BaSnO$_3$ is, therefore, simultaneously sensitive to both O$_2$ and H$_2$O, as shown by the weight change results, Fig.4. The sample used for Fig. 4 was slow-cooled from 1300 °C and left exposed to laboratory air for several days prior to weight change studies as a function of temperature on heating. Data up to ~ 800 °C were not reproduced on subsequent stepwise cooling and, without prolonged storage at room temperature, on second heating; they are therefore, attributed to loss of water from the original sample.

BaSnO$_3$ is reported to be n-type [15,24], especially when processed under reducing conditions [6,7,11,14,21,27] and is associated with oxygen deficiency, eq’n (3). Our results on the sensitivity of conductivity to pO$_2$ are fully consistent with this, although the level of n-type conductivity is much less in samples prepared in air at high temperatures that have
smaller oxygen deficiency. Acceptor-doped BaSnO$_3$ is, however, p-type as are some of the reported undoped samples [12]. The conduction mechanism, whether p- or n-type is critical for sensor action in those cases where sensitivity is controlled by the effect of changing pO$_2$. Thus, the effect of reducing gases on the conductivity is the exact opposite for n- and p-type BaSnO$_3$.

Conclusions

- BaSnO$_3$ loses a small amount of oxygen spontaneously and reversibly at high temperature. The oxygen content depends on temperature and almost certainly, on pO$_2$, as shown by literature reports on the effect of heating in vacuum.

- Oxygen-deficiency of samples prepared at high temperatures can be preserved by quenching, but partial or complete re-oxidation occurs on annealing at lower temperatures.

- Oxygen-deficient samples are also sensitive to moisture; the observed increase in conductivity in a wet atmosphere is attributed to proton conduction.

- Oxygen-deficient samples show high and rapid sensitivity to pO$_2$ over a range of temperatures. Sensitivity of oxidized samples to N$_2$ and CO$_2$ is similar, probably because the main factor causing sensitivity is the reduction in pO$_2$ rather than the interaction of (dry) N$_2$ or CO$_2$ with the sample surface. According to [12], sensitivity to CO$_2$ is favoured by a moist atmosphere, indicating a sensor mechanism associated with carbonate formation.

- The mechanism of sensitivity to pO$_2$ appears not to involve Schottky barriers. Instead, O$_2$ adsorption / desorption at / from sample surfaces leads to a change in bulk conductivity of the sample rather than to a modification of Schottky barriers heights, for which there is no evidence in the impedance data.

- BaSnO$_3$ is usually reported to be a modest, n-type semiconductor. The semiconductivity may be associated with a small, residual oxygen deficiency, depending on synthesis conditions.
The activation energy for electronic conduction found here is usually in the range 0.8-1.1 eV, depending on sample history; these values are significantly less than half the intrinsic band gap, ~ 3.5 eV, which suggests that the carriers occupy localised states within the band gap.

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29- Sensitivity is taken as the magnitude of the difference in resistance in N₂ and O₂, i.e R(O₂)-R(N₂); the rate of change of resistance is not included in this assessment