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Journal of the European Ceramic Society 27 (2007) 285–290

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Propane gas sensing with high-density $SrTi_{0.6}Fe_{0.4}O_{(3-\delta)}$ ceramics evaluated by thermogravimetric analysis

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Received 28 January 2006; received in revised form 25 April 2006; accepted 6 May 2006
Available online 15 June 2006

Abstract

Semi-conducting $SrTi_{0.6}Fe_{0.4}O_{(3-\delta)}$ in the form of porous thick films might be of interest as a novel material for resistive hydrocarbon sensor applications. As the underlying gas-sensing mechanism is still a matter of question, thermogravimetric analysis was performed on high-density (≥99%) $SrTi_{0.6}Fe_{0.4}O_{(3-\delta)}$ ceramic specimens in order to investigate whether bulk properties are affected by the catalytic oxidation of propane at the material surface. At temperatures 250–400 °C, bulk oxygen content was found to significantly decrease upon exposure to traces of propane (0–3000 ppm) in a background of 20% O_2/80% Ar. Lattice oxygen is sufficiently mobile in this compound so that reducing surface reactions are followed by a bulk redox reaction even at low or moderate temperatures. Concomitant changes in the electrical resistance of dense ceramics are consistent with this picture. The hydrocarbon sensitivity of $SrTi_{0.6}Fe_{0.4}O_{(3-\delta)}$ artifacts seems thus to a large extent to be correlated to modifications in the bulk defect chemistry of the material.

Keywords: Sintering; Perovskites; Sensors; $Sr(Ti,Fe)O_3$; Propane

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1. Introduction

Recently, it has been reported that the electrical resistance of porous thick films[1] and polycrystalline thin films[1,2] based on semi-conducting compounds in the $SrTi_{(1-x)}Fe_xO_{(3-\delta)}$ system is sensitive to traces of hydrocarbon gases in the surrounding atmosphere. These non-stoichiometric oxides which exhibit a p-type conducting behavior at elevated temperatures and under oxidizing conditions[3,4] thus appear to be of interest as novel materials for application as resistive hydrocarbon gas sensors. There are various ways in which reactive gaseous species can affect the electrical conductivity of oxide materials,[5–8] but in the case at hand some open questions remain with respect to the underlying gas-sensing mechanism, i.e. is it due to surface- or bulk-related phenomena.

The sensitivity of semi-conducting oxides towards trace reducing gases in an otherwise oxidizing atmosphere can formally be explained by a simple model.[5] When reducing agents reach catalytically active surfaces of oxide materials, they irreversibly react with chemisorbed and/or lattice oxygen in the outermost surface layers. Thus, there is an interference with interfacial exchange reactions between gaseous oxygen and surface oxygen species which try to maintain the equilibrium state at the surface of the oxide. If the catalytic oxidation of the reducing gas by oxygen from the surface proceeds fast enough, the prevailing equilibrium is effectively perturbed and a new non-equilibrium state can be established that is characterized by a kinetically determined decrease in the concentration of negatively ionized surface oxygen species. As a consequence, charge is transferred to the oxide which can give rise to modifications in the electrical resistance of the material. Resistance changes are thus dependent upon the ratios of the rate constants for the involved surface reactions.[5]

Oxide-based, solid-state gas sensors for trace reactive gases typically operate at temperatures below 500 °C.[6] If lattice oxygen anions are immobile at the sensor operating temperature, resistance will only be modified to a certain depth at the surface. In this case, $SrTi_{(1-x)}Fe_xO_{(3-\delta)}$ would work as a gas-sensitive resistor provided the material is present in a high surface-to-bulk form, viz. artifacts with open porosity or very thin, dense films. If, however, lattice oxygen anions are sufficiently mobile, surface reactions are followed by a change in bulk oxygen con-

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doi:10.1016/j.jeurceramsoc.2006.05.078

tent and the resistance of the entire artifact becomes modified. In this case, $SrTi_{(1-x)}Fe_xO_{(3-\delta)}$ would work as a gas-sensitive resistor even though the material is present in a high-density form. A good indicator of such a type of response would be the weight loss resulting from the oxygen departure from the sensor sample.[9]

Previous studies[10–12] have shown that the oxygen content of compositions in the $SrTi_{(1-x)}Fe_xO_{(3-\delta)}$ system can be altered by means of thermal treatments at temperatures ≤500 °C. Kumar and Post[2] assume on the basis of their thermogravimetric measurements on $SrTi_{0.6}Fe_{0.4}O_{(3-\delta)}$ powder samples at 450 °C that the oxidation of hydrocarbons occurs with the source of oxygen both from the gas phase and from the lattice. These findings indicate that lattice oxygen is mobile at those temperatures which are of interest for the operation of resistive $SrTi_{(1-x)}Fe_xO_{(3-\delta)}$ hydrocarbon gas sensors.

The aim of the present work was thus to investigate whether bulk properties of high-density $SrTi_{(1-x)}Fe_xO_{(3-\delta)}$ ceramic specimens are affected by the catalytic oxidation of hydrocarbons at the materials surface at temperatures below 500 °C. The concern was to gain some insight into the mechanism underlying the sensor operation of porous thick films and thin films. In order to compare the outcome of the present study with previously published data, work has focused on one particular composition, $SrTi_{0.6}Fe_{0.4}O_{(3-\delta)}$, and propane gas was selected as the reducing agent. Thermogravimetric analysis (TGA) was used to evaluate changes in oxygen deficiency and DC resistance measurements were employed to trace changes in the electrical properties of the material.

2. Experimental

The starting ceramic powder of $SrTi_{0.6}Fe_{0.4}O_{(3-\delta)}$ (STF40) was prepared by solid-state reaction from titanium and iron oxides and strontium carbonate. Appropriate amounts of the reactants were mixed together and calcined at 1200 °C for 15 h in air. The resulting material was then finely ground by ball milling. Using light scattering (Mastersizer Microplus, Malvern Instruments), the mass median diameter of the powder particles was found to be approximately 1.9 μm.

From this powder, cylindrical greens of diameter 13 mm and height 7 mm were formed by cold isostatic pressing at 850 MPa. Before pressing, the powder was granulated by adding a liquid organic binder (Optapix PAF 35, Zschimmer and Schwarz, 3 wt.% addition) in order to enhance the fracture strength of the green bodies. The binder was completely burnt off before sintering by firing at 800 °C for 10 h in air.

Sintering of the samples was performed in a tube furnace according to the following schedule: The powder compacts were heated to 1400 ± 10 °C at a rate of 5 °C/min under a flow of pure oxygen and sintered for another 6 h at this temperature; afterwards, oxygen was replaced with argon (measured oxygen content: 70 ± 20 ppm) and the samples were cooled down to room temperature at a rate of 1 °C/min. This sintering procedure was chosen because it was repeatedly found that the ceramics had developed cracks when they were cooled down under oxidizing conditions. The unit cell of $SrTi_{(1-x)}Fe_xO_{(3-\delta)}$ compounds contracts with progressing oxidation.[10,11] Upon reducing the temperature in oxidizing atmospheres, stresses can appear within large and dense ceramic bodies that can lead to the initiation of cracks. A similar behavior was reported in a study on the sintering behavior of $Sr(Fe,Co)O_{(3-\delta)}$ ceramics and was discussed in detail therein.[13]

The material was characterized by means of powder X-ray diffraction (XRD) measurements on crushed samples. Patterns were recorded at room temperature with a Philips MRD diffractometer in the Bragg–Brentano configuration using Cu Kα radiation ($K\alpha_2/K\alpha_1$ intensity ratio: 0.5) and a graphite diffracted-beam monochromator. The microstructure was checked by scanning electron microscopy (SEM) (Hitachi S-4100) on polished and thermally etched cross sections of the ceramics. For this purpose, smooth surfaces were prepared by polishing with diamond particles with sizes down to 1 μm. Thermal etching was performed at 1250 °C for 1 h in air.

Specimens for the TGA and DC resistance measurements were prepared by cutting the sintered bodies into thin discs of size ≈ 6 mm × 6 mm and thickness 400–500 μm. All faces were slightly polished with SiC paper of grit size P1000 to remove surface roughness and/or contaminated surface layers. Afterwards, the discs were ultrasonically cleaned in acetone for 10 min. As the material had been cooled down in argon after sintering, a considerable oxygen deficiency was to be expected. Therefore, all discs were subjected to a re-oxidation treatment before employing them for the studies. This was accomplished by slowly heating the discs at a rate of 0.5 °C/min to 400 °C and slowly cooling them down at the same rate to room temperature in a mixture of 20% O_2/80% Ar; the amounts of oxygen absorbed during this treatment were determined by weighing.

TGA measurements were conducted with a Netzsch 439 TGA system where the specimens could be exposed to gas flows of varying composition. DC resistance measurements were done in a home-made open flow system employing a four-point probe technique. As electrical leads, platinum wires were attached to four points at the circumference of the samples using silver paste. For both types of experiments a mixture of 20% O_2/80% Ar was used as the reference gas. The propane concentration could be adjusted by admixing defined amounts of a prefabricated mixture of 1% propane/99% Ar; total gas flow was always set to 100 ml/min.

3. Results and discussion

3.1. Characterization of the material

Fig. 1(pattern (a)) shows the XRD pattern of a powdered STF40 ceramic that was sintered according to the described schedule. The as-prepared material crystallized in the expected cubic perovskite structure[14,15] and was – within the detection limit of XRD – free of second phases. A lattice parameter of 0.3909(2) nm could be derived from the pattern by means of profile matching using the FULLPROF[16] program. Density of the sintered pellets was determined by the Archimedes method using de-ionized water and values of about 5.09 g/cm^3 were found. Fig. 2 presents an SEM image of a polished and thermally

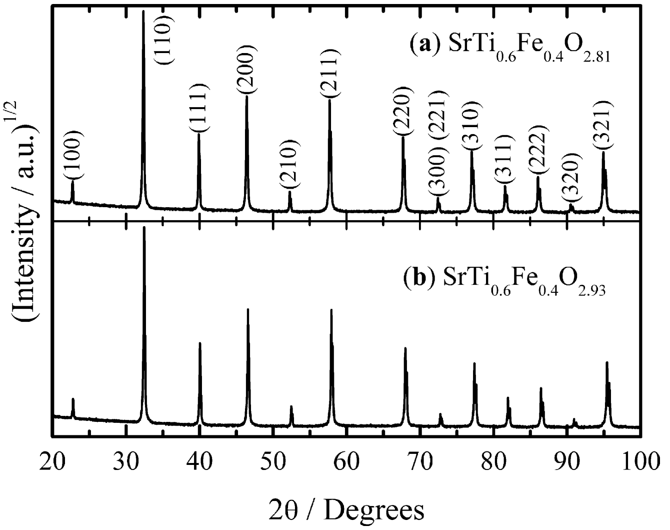

Fig. 1. Room temperature X-ray diffraction patterns of powdered STF40 ceramics that were sintered at 1400 °C for 6 h in oxygen and cooled down to room temperature at 1 °C/min in argon: (a) before and (b) after a re-oxidation treatment in a mixture of 20% O_2/80% Ar (specified oxygen content: see text).

etched cross section of a pellet. The micrograph demonstrates that the ceramics were very dense consisting of grains with sizes in the range 2–8 μm.

As mentioned above, all specimens for the measurements were heat-treated in a mixture of 20% O_2/80% Ar to compensate for the oxygen deficiency. After the re-oxidation runs, the mass of the STF40 discs had increased by 1.03(2)% and the color of the material had changed from dark brown to black. The re-oxidized material exhibited the same cubic perovskite structure as before (pattern (b) in Fig. 1), but oxygen uptake was accompanied by a decrease in lattice parameter as seen from the shift of the diffraction peaks towards higher 2θ values. By means of profile refinement, a lattice parameter of 0.3895(2) nm was derived from the XRD pattern. This value is in good agreement with those values found for STF40 material subjected to sintering treatments in air.[14,17]

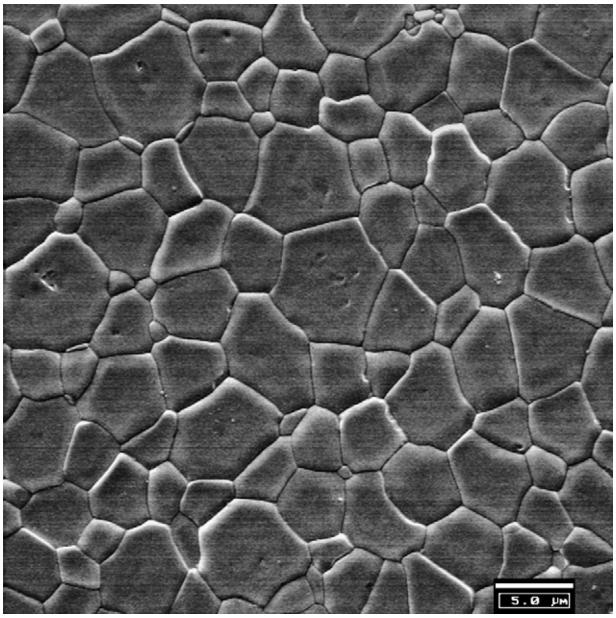

Fig. 2. SEM micrograph of a polished and thermally etched cross section of an STF40 ceramic pellet that was sintered at 1400 °C for 6 h in oxygen and cooled down to room temperature at 1 °C/min in argon (marker length: 5 μm).

The oxygen stoichiometry of the STF40 ceramics was estimated on the basis of previously published data. Zhou and Goodenough[17] give a value of 2.94(1) for the oxygen content $(3-\delta)$, of the composition $SrTi_{0.6}Fe_{0.4}O_{(3-\delta)}$ that was processed in air during sintering and a value of 2.92 is reported in a publication by Zhuang et al.[18] On the assumption that the re-oxidized material at hand had attained a comparable oxidation state $(3-\delta) = 2.93$, the oxygen deficiency, δ, of the as-prepared material could be re-calculated from the measured weight gains and thus amounted to approximately 0.19.

Taking into account the weight gain and unit cell contraction upon re-oxidation, the density of the re-oxidized STF40 ceramics was about 5.20 g/cm^3. To calculate the theoretical density one has to resort to data from other groups. For $SrTi_{0.6}Fe_{0.4}O_{2.94}$ a lattice parameter of 0.3893(1) nm can be taken from Fig. 2 in the publication by Zhou and Goodenough.[17] Adopting this value, the theoretical density is calculated to be ≈5.23 g/cm^3. The STF40 ceramics as presented here thus featured very high densities.

3.2. Gas-sensing properties

3.2.1. Thermogravimetric analysis

The fact that oxygen-deficient STF40 ceramics can be re-oxidized at temperatures below 400 °C already proves that lattice oxygen is mobile at those temperatures which are of interest for sensor applications. Further evidence was provided by TGA measurements on re-oxidized STF40 ceramic specimens that were performed in order to obtain more information on the reduction/oxidation behavior. Representative results are shown in Fig. 3 displaying the weight change characteristic of a thin

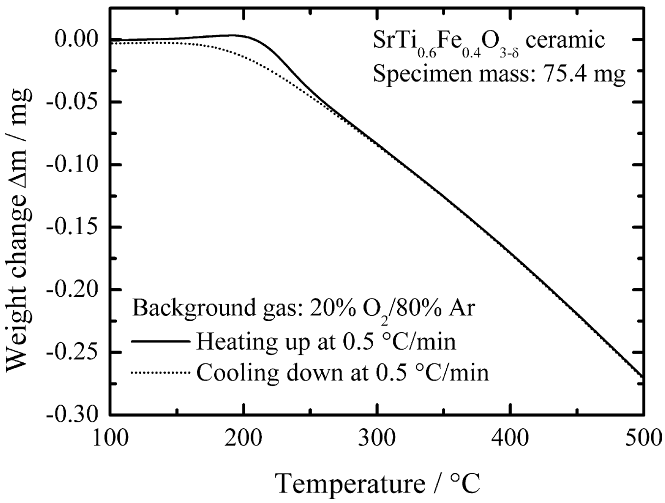

Fig. 3. Weight change characteristic of an STF40 ceramic disc of mass 75.4 mg and thickness 415 ± 20 μm as a function of temperature obtained on heating up (solid line) and cooling down (dotted line) at 0.5 °C/min in a background of 20% O_2/80% Ar.

disc of mass 75.4 mg and thickness 415 ± 20 μm (geometric surface area: ≈0.75 cm^2) as a function of temperature obtained on heating up (solid line) and cooling down (dotted line) at rates of 0.5 °C/min in the background atmosphere of 20% O_2/80% Ar.

Above about 200 °C, the sample weight changed with changing temperature due to the release/uptake of oxygen. In the temperature range 250–500 °C, no hysteresis between the heating and cooling cycle could be observed. Hence, heating and cooling rates of 0.5 °C/min were low enough for the STF40 ceramic specimen to reach its equilibrium oxygen content in the ambient atmosphere. Differences appeared at temperatures below about 250 °C. The processes that control oxygen release/uptake – interfacial exchange reactions and/or solid state diffusion – became too sluggish to achieve complete equilibration under the selected experimental conditions.

The measurement clearly demonstrates that the mobility of lattice oxygen is sufficiently high to allow the whole volume of the STF40 material to respond to varying outside conditions at temperatures far below 500 °C. Previous findings[10–12] could thus be confirmed. High oxygen diffusivities even at low or moderate temperatures do not seem to be surprising in the case of compounds in the $SrTi_{(1-x)}Fe_xO_{(3-\delta)}$ system. It has been reported in various studies[19–21] that the formation of microdomains is not an unusual characteristic of non-stoichiometric perovskite-related oxides. Domain walls are potential short-circuit pathways for oxygen diffusion. Overall reduction/oxidation processes can thus be accelerated as a result of long-range fast oxygen transport along microdomain walls, followed by slow diffusion over short distances within the domains.[19]

Significant differences in the weight change characteristic occurred when STF40 ceramic specimens were heated up in atmospheres with or without the addition of low amounts of propane. Typical results of some measurements on the specimen discussed above – illustrated as changes in the oxygen deficiency $(3-\delta)$ – are shown in Fig. 4. The solid line depicts the oxygen stoichiometry as a function of temperature obtained on heating to 500 °C at a rate of 0.5 °C/min in the pure reference atmosphere. The data were calculated from the measured weight changes by adopting a reference value of $(3-\delta) = 2.93$ at room temperature.

The dashed and dotted lines in Fig. 4 represent results of similar measurements on the same specimen by the time the propane concentration in the reference gas has been adjusted to 1500 and 3000 ppm, respectively. During these runs, exposure to propane was only allowed while the temperature was raised. After reaching the maximum temperature, the propane gas was switched off and the specimen was cooled down to room temperature at a rate of 0.5 °C/min in the pure reference gas. By this means, the specimen was recharged with oxygen in order to ensure the same initial conditions for subsequent measurements.

It is quite obvious from Fig. 4 that the presence of low amounts of propane gives rise to pronounced deviations from the reference or equilibrium measurement (solid line) at temperatures 250–400 °C. The oxidation of propane by oxygen from the surface of the specimen thus proceeds fast enough to effectively interfere with the equilibration process within this temperature range. Concentration of surface oxygen species is lowered compared to that in the reference state becoming manifest in an additional reduction of the material.

Presuming a surface oxygen density of about 10^{15}/cm^2, the propane-induced changes in the oxygen content cannot be explained solely by a partial reduction of one or two surface layers of the ceramic specimen, even if one assumes that the real surface area is 100 times larger than the geometric one. Hence, the additional decrease in oxygen content is related to a bulk redox mechanism: the partial reduction of the outermost surface layers owing to fast catalytic reactions with propane is not limited to the surface itself but progresses into the bulk in that lattice oxygen anions diffuse out of the material thus participating in the oxidation of the trace reducing agent. Such a behavior is not an unusual finding; oxidation reactions of propylene over a certain class of metal oxide catalysts – among them Fe_2O_3 – have also been recognized as proceeding by a bulk redox mechanism at moderate temperatures.[22]

It should be emphasized here that one is faced with a system that is driven into a real non-equilibrium steady-state. The additional reduction of the material at temperatures 250–400 °C would under no circumstances have any relation to slight shifts in oxygen partial pressure because of potential gas-phase reactions between gaseous oxygen and propane. It is merely an outcome of a locally reduced oxygen activity at the material surface because of very fast catalytic surface reactions with the trace reducing agent. By this way, a driving force for an outward flux of lattice oxygen is constituted until a stationary state is reached.

The progression of the "non-equilibrium" curves (see Fig. 4) at lower temperatures might indicate that the catalytic activity of the STF40 surface rapidly increases with increasing temperature. At temperatures 300–320 °C, the catalytic surface reaction with propane exerts its maximal influence – in relation to the reference measurement – on the bulk oxygen content of the material. Above about 320 °C, the "non-equilibrium"

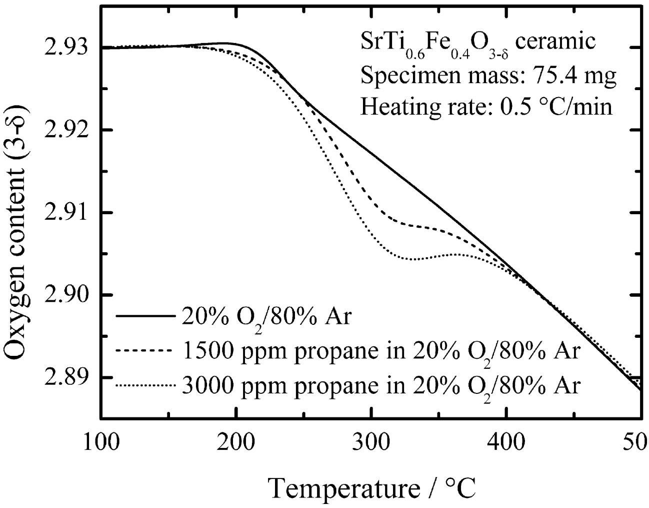

Fig. 4. Oxygen content of an STF40 ceramic disc of mass 75.4 mg and thickness 415 ± 20 μm as a function of temperature obtained on heating up at 0.5 °C/min in a background of 20% O_2/80% Ar (solid line) and in background atmospheres of 1500 ppm (dashed line) and 3000 ppm propane (dotted line) in 20% O_2/80% Ar.

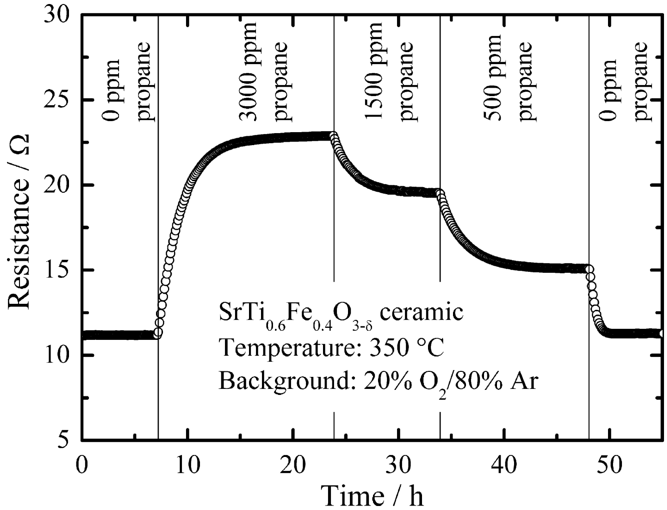

Fig. 5. Resistance response of an STF40 ceramic disc of thickness 480 ± 20 μm at 350 °C to varying concentrations of propane in a background of 20% O_2/80 % Ar (measuring current: 8 mA).

curves begin to approach the reference curve with increasing temperature. This may be an indication that the interfacial exchange reactions between surface oxygen species and gaseous oxygen now become fast enough to gradually overcome the influence of the trace reducing agent so that the equilibrium state can be re-established. As the overall run of the "non-equilibrium" curves results from a complex interplay between various processes that take place at the surface of the STF40 material (adsorption/desorption, chemical and charge transfer reactions) and within the material (solid-state diffusion), modeling of the results was beyond the scope of the present work.

3.2.2. DC resistance measurements

The outcome of the TGA measurements suggests that the response mode of gas-sensitive STF40 resistors is actually related to a bulk redox mechanism. Jurado et al.[23] have shown that the electrical behavior of polycrystalline $Sr_{0.97}Ti_{(1-x)}Fe_xO_{(3-\delta)}$ materials with moderate or high Fe contents is dominated by bulk properties, i.e. grain boundary effects play no or only a secondary role. Bulk resistivity of p-type conducting compounds in the $SrTi_{(1-x)}Fe_xO_{(3-\delta)}$ system should increase on lowering the oxygen content because holes are consumed in this way.[3,4,24] One can thus anticipate that traces of propane in an otherwise oxidizing atmosphere will lead to a marked increase in the resistance of high-density STF40 ceramic specimen as a consequence of modifications in the bulk defect chemistry of the material.

Fig. 5 displays the resistance response of an STF40 ceramic disc of thickness 480 ± 20 μm at 350 ± 5 °C while altering the propane concentration in the reference gas. Since the TGA measurements indicated a sufficiently high sensitivity at 350 °C, this operating temperature was selected to ensure reasonable transient response times. Before the measurement, the sample was slowly heated up to 350 °C at a rate of 0.5 °C/min to allow for equilibration in the reference gas atmosphere. Measurement was started when sample resistance had achieved its steady value.

It is seen from Fig. 5 that exposure to low amounts of propane led to the expected increase in specimen resistance. The response took a much longer time than in the case of screen-printed thick films[1] with open porosity and particle sizes of approximately 2 μm. It can therefore be inferred that in the case of dense ceramics oxygen release/uptake is to a large extent controlled by solid-state diffusion. The ascertained gas sensitivities (relative resistance changes) are comparable to, but somewhat lower than those measured on porous artifacts. At a propane concentration of 500 ppm, for example, values of 0.35–0.40 were obtained for STF40 ceramic specimens at 350 °C (Fig. 5), whereas the sensitivity of porous thick films was found to be about 0.9 under the same conditions (taken from Fig. 8 in the publication by Sahner et al.[1]).

The impedance of porous artifacts, in general, is due to two components: first, the bulk resistance and second, the resistance of intergranular boundaries. The rough agreement between the gas sensitivities of dense ceramics and porous thick films points out that bulk resistance changes upon exposure to propane make a significant contribution to changes in the overall resistance of STF40 artifacts.

Differences in gas sensitivity could also be explained by the fact that the effectiveness of solid-state gas sensors depends on several factors including the catalytic properties of the surface. Surface defect chemistry plays a decisive role since it mediates the sensor response of the material.[5,25] As the surface chemistry is to a large extent governed by the state of the surface formed as a result of segregation,[26] it will be affected by the processing history of the material. It is therefore quite understandable that gas sensors which are made from one and the same compound by means of, however, diverse preparation processes differ in absolute sensitivity even though the underlying gas-sensing mechanism is the same.

4. Conclusions

The outcome of the present work shows that thermogravimetric analysis on dense ceramic specimens is a useful method for evaluating new gas-sensitive oxide materials with respect to the underlying gas-sensing mechanism. It has been demonstrated by measurements on $SrTi_{0.6}Fe_{0.4}O_{(3-\delta)}$ ceramics in a high-density form that catalytic surface reactions with traces of propane affect the oxygen content of the material at those temperatures which are of interest for hydrocarbon sensor applications. The chemical diffusivity of lattice oxygen in this compound is sufficiently high so that surface reactions are followed by a bulk redox reaction even at relatively low temperatures. As a result, the electrical resistance of dense ceramics is sensitive to traces of propane, too. On the assumption that other compositions in the $SrTi_{(1-x)}Fe_xO_{(3-\delta)}$ system behave in a similar manner, it can be concluded that bulk-related phenomena have to be taken into account when one is aiming at a thorough understanding of the gas-sensing behavior of these materials.

Acknowledgements

The author is thankful to Prof. R. Waser (Forschungszentrum Jülich GmbH), Prof. R. Moos and K. Sahner (both from Universität Bayreuth, Germany) for fruitful discussions. He also thanks K. Sahner for providing the starting STF40 powder and J. Friedrich and H. Bierfeld (both from Forschungszentrum Jülich GmbH) for technical assistance. Financial support for this project by a joint international program of the Helmholtz Gemeinschaft (Germany) and the National Research Council of Canada is gratefully acknowledged (project 01SF0201/9.1).

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