NRC Publications Archive Archives des publications du CNRC

Thin films of non-stoichiometric perovskites as potential oxygen sensors

Post, Michael L.; Sanders, Brian W.; Kennepohl, P.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

[https://doi.org/10.1016/0925-4005\(93\)85379-O](https://doi.org/10.1016/0925-4005(93)85379-O)

Sensors and Actuators B: Chemical, 13, 1-3, pp. 272-275, 1993-05

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=ed74cb9b-9a8c-467f-a8b2-e96e79f80df8>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=ed74cb9b-9a8c-467f-a8b2-e96e79f80df8>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Thin films of non-stoichiometric perovskites as potential oxygen sensors

Michael L. Post, Brian W. Sanders and P. Kennepohl*

Institute for Environmental Chemistry, National Research Council of Canada, Montreal Road, Ottawa, Ont., K1A 0R6 (Canada)

Abstract

Thin films of non-stoichiometric perovskites of general formula $\text{ABO}_{2.5+x}$ have been grown, on sapphire substrates, by the technique of pulsed laser ablation/deposition. The structural properties of the films upon exposure to atmospheres of various oxygen pressures, at elevated temperatures, have been determined by X-ray diffraction; they show changes which correlate with those found for bulk powder samples. For the material $\text{SrFeO}_{2.5+x}$, with $0 \leq x \leq 0.5$, pressure–composition isotherms reveal several pressure ranges over which structural changes occur. By monitoring the changes in physical properties that accompany the bulk chemical changes, this system can be exploited to provide a thin-film sensor, the structural changes of which are specific to oxygen.

Introduction

Metal oxides and materials that are related by doping metal oxides with one or more of a diverse selection of metallic elements have found application in many gas-sensing areas [1, 2]. Perovskites, with the general formula ABO_3 , where A and B are metals, are just one of many structural families of metal oxides which have recently received increased attention in sensor science [3, 4]. However, in all cases it is the surface reactivity that induces the sensor response, and since the chemistry tends to be non-specific and of oxidative/reductive character, the consequence is a lack of specificity for the detection of analytes that have similar redox chemistry. However, perovskites with the A and B elements judiciously chosen, and typically with B stable in two or more oxidation states within the structure, can exhibit significant non-stoichiometry of oxygen [5]. From a sensor viewpoint the non-stoichiometry, and the compositional variation within the range defined by its limits, can be explored for chemical and associated physical changes that offer measurable property changes for sensor purposes.

The current work is directed toward identifying perovskites which offer a specific chemistry for an analyte gas. Reported here are results obtained for the material $\text{SrFeO}_{2.5+x}$, which has a compositional range $0 \leq x \leq 0.5$ [6], and which shows behaviour that makes it an excellent candidate as a gas-specific oxygen sensor. Structural

and thermodynamic data are presented for the system $\text{SrFeO}_{2.5+x} + \text{O}_2$ at temperatures $400 \leq T \leq 700$ K, and for the perovskite in bulk powder form. Conditions for the formation of thin films of $\text{SrFeO}_{2.5+x}$, by using the technique of pulsed laser ablation/deposition, are also described. Structural changes of the thin films upon exposure to oxygen are correlated with data obtained for the corresponding bulk powder state.

Experimental

Samples of $\text{SrFeO}_{\sim 3}$ were prepared by sintering intimately mixed stoichiometric quantities of SrCO_3 and Fe_2O_3 (Johnson-Matthey, Puratronic grade, 99.999% purity) in an alumina crucible at $T=1520$ K in air or oxygen. The sintering process was repeated until powder X-ray diffraction indicated a single-phase product. Trace elemental analysis was done by ICP-mass spectrometry, which confirmed sample purity. X-ray data were obtained on a Scintag P2000 diffractometer, operating with graphite monochromated Cu K_α radiation.

Thermodynamic data for the reaction of bulk powder $\text{SrFeO}_{2.5+x}$ with oxygen were collected as pressure–composition (p – x) isotherms within the temperature and pressure ranges $400 \leq T \leq 800$ K and $0 \leq p(\text{O}_2) \leq 0.2$ MPa, respectively. Oxygen was added stepwise to $\text{SrFeO}_{\sim 2.5}$ in a volume-calibrated apparatus constructed of stainless steel, and equipped with vacuum and an oxygen source and a high-accuracy capacitance pressure transducer. To confirm reversibility, oxygen desorption isotherms were also measured using samples

*Present address: Department of Chemistry, Concordia University, Montreal, Quebec, H4B 1R6, Canada.

which had reached the maximum stoichiometry. Stoichiometry changes in the solid phase were calculated by using volumetric measurements of the gas phase, with an accuracy of ± 0.01 in x . Temperature control and data acquisition were under computer control. Other details of the apparatus are described elsewhere [7].

Thin films of the parent perovskite were grown by the technique of pulsed laser ablation/deposition in a controlled-atmosphere chamber equipped with a target and heated substrate holders. An excimer laser (KrF; $\lambda = 248$ nm) pulsed at 10 Hz and with its output focused to give a fluence of between 1 and 2 J cm⁻² at the target was used as an energy source. Films were grown from targets made as sintered pellets of composition SrFeO_{2.5+x} with $x = 0$ and $x \sim 0.5$, in atmospheres ranging from vacuum ($p(\text{O}_2) < 1.3 \times 10^{-4}$ Pa) or $p(\text{O}_2) \sim 40$ Pa, and deposited upon substrates of single-crystal sapphire with (1102) orientation. The sapphire was heated to temperatures in the range $450 \leq T \leq 1150$ K, and held isothermal during deposition. Deposition times of about 20 min produced films of 300 nm thickness. Films were subsequently cooled in the chamber in atmospheres ranging from vacuum to $p(\text{O}_2) \sim 100$ kPa. The phase purity was determined by X-ray diffraction, and some aspects of the morphology, metal stoichiometry and optical properties of the films were evaluated by SEM, XPS and UV-Vis spectroscopy. After deposition, treatment of the films in various pressures of O₂ at temperatures $400 \leq T \leq 800$ K was achieved in a batch mode using an apparatus as described above for the bulk material. The film properties were then re-evaluated.

Results and discussion

A p - x isotherm for the reaction of SrFeO_{2.5+x} with oxygen at $T = 520$ K is shown in Fig. 1, together with a reduced phase diagram for the SrFeO_{2.5+x} + O₂ system; the data agree with those reported [6] for the existence of the phases described as orthorhombic-brownmillerite (BR), orthorhombic-perovskite (OP), tetragonal-perovskite (TP) and cubic-perovskite (CP). X-ray data for SrFeO_{2.5+x} in bulk powder form for $x = 0$, 0.36 and ~ 0.5 are shown in Fig. 2, and these correspond to BR, TP and CP structures, respectively. Figure 3 shows an X-ray spectrum of a thin film grown at $p(\text{O}_2) = 25$ Pa compared with that of the bulk material having $x \sim 0.5$. The film is clearly crystalline, and exhibits strong preferential orientation upon deposition. By comparison with bulk X-ray spectra, the reflection positions of the dominant (110) and (200) planes show that the film is in the CP form. When films are grown under vacuum, or close to vacuum condition, the oxygen-depleted ($x = 0$) BR form is produced with the characteristic split re-

Fig. 1. p - x isotherm (lower curve) for SrFeO_{2.5+x} + O₂ at $T = 520$ K, and the reduced phase diagram (upper curve) for this system. Phases are identified as: BR, orthorhombic-brownmillerite; OP, orthorhombic-perovskite; TP, tetragonal perovskite; CP, cubic-perovskite.

Fig. 2. X-ray diffraction spectra of bulk powder samples of SrFeO_{2.5+x} taken with monochromated Cu K α radiation. The spectra shown are for $x = 0$, 0.36 and ~ 0.5 , corresponding to the BR, TP and CP forms, respectively.

flections near $2\theta = 32^\circ$ (Fig. 4). The films, whether produced under conditions favouring oxygen-depleted or oxygen-rich compositions, can be treated following

Fig. 3. X-ray diffraction spectra of SrFeO_{3-x} as powder and thin film on (1102)-oriented sapphire. The film exhibits (110) and (100) preferential orientation. The cusp in the upper curve at $2\theta \approx 53^\circ$ is due to the sapphire substrate.

Fig. 4. X-ray diffraction spectra of the (110) region of $\text{SrFeO}_{2.5+x}$ for powder and thin-film samples. The upper pair of curves shows the BR structure; the lower pair shows the CP form.

deposition to produce the CP structural form from the BR form, and vice versa, as shown in Fig. 4. Reversibility has been demonstrated at temperatures as low as $T = 420$ K; however, the reaction kinetics in films at these temperatures have not yet been directly measured. For a bulk powder sample at $T = 420$ K, the reaction is 90% complete within 30 s.

The ratio of the limits of $p(\text{O}_2)$ over which structural changes occur defines a dynamic range for the use of these materials as an oxygen sensor. This quantity is close to 10^4 for $T = 520$ K (Fig. 1), with an upper limit $p(\text{O}_2) \approx 0.2$ MPa. Because the full composition limits in $\text{SrFeO}_{2.5+x}$ encompass four phase regions, it is anticipated that the transduction signal will not have linear response to oxygen concentration over the whole dynamic range. However, selecting the operational tem-

perature of the film ensures that for some compositional ranges, a segment of the phase diagram can be chosen to optimize the sensor to the $p(\text{O}_2)$ of the analyte gas stream. The film properties currently being evaluated as a transduction signal for sensor response include electrical resistance, optical transmission and mass-loading effects with bulk or surface acoustic wave techniques.

Conclusions

Thin films of $\text{SrFeO}_{2.5+x}$ exhibit reversible oxygen absorption, which results in structural modifications that correlate with those found for the bulk powder material. The changes that occur in the crystal structure of the films are, therefore, unique to oxygen and hence the material is suitable for use as a gas-specific oxygen sensor.

References

1. T. Seiyama (ed.), *Chemical Sensor Technology*, Vol. 1, Kodansha, Tokyo, Elsevier, Amsterdam, 1988, and articles therein.
2. N. Yamazoe, New approaches for improving semiconductor gas sensors, *Proc. 3rd Int. Meet. Chem. Sensors, Cleveland, OH, USA, Sept. 14-16, 1990*, pp. 3-8.
3. N. Koshizaki, K. Suga and K. Yasumoto, Gas sensing characteristics of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ and related compounds, *Proc. 3rd Int. Meet. Chem. Sensors, Cleveland, OH, USA, Sept. 14-16, 1990*, pp. P57-P58.
4. Z. Zhigang and Z. Gang, BTS: A new ferroelectric for multifunctional sensors, *Ferroelectrics*, **101** (1990) 43-54.
5. C. N. R. Rao, J. Gopalakrishnan and K. Vidyasagar, Superstructures, ordered defects and nonstoichiometry in metal oxides of perovskite and related structures, *Indian J. Chem.*, **23A** (1984) 265-284.
6. J. B. MacChesney, R. C. Sherwood and J. F. Potter, Electric and magnetic properties of the strontium ferrates, *J. Chem. Phys.*, **43** (1965) 1907-1913.
7. M. L. Post and J. J. Murray, Mg_2Ni hydride: in situ heat conduction calorimetry of the phase transition near 510 K, *J. Less-Common Met.*, **134** (1987) 15-26.

Biographies

Michael L. Post obtained a B.Sc. in 1968 and a Ph.D. in 1971, both from the University of Surrey. He is presently employed by the National Research Council of Canada as a senior research officer. His fields of interest include chemical sensors, solid-state reaction chemistry, X-ray crystallography and reaction calorimetry.

Brain W. Sanders obtained a B.Sc. from the University of Guelph in 1984, an M.Sc. from the University of Guelph in 1986, and a Ph.D. from McMaster University

in 1991. His present employment is at the National Research Council of Canada as a research associate. His fields of interest include chemical sensors, thin-film deposition and characterization, electroluminescence and thin-film solar cells.

Pierre Kennepohl received a B.Sc. from Concordia University in 1992. He is currently a research assistant at Argonne National Laboratories, and hopes to begin graduate studies shortly. His fields of interest include chemical sensors and nuclear chemistry.