Study of non-stoichiometric BaSrTiFeO$_3$ oxide dedicated to semiconductor gas sensors

D. Fasquelle$^a$, N. Verbrugghe$^a$, S. Députier$^b$

$^a$Unité de Dynamique et Structure des Matériaux Moléculaires (UDSMM)
Université du Littoral Côte d'Opale, 50 rue F. Buisson, BP717, 62228 Calais, France
Tel/fax: 00 33 21 46 57 78

$^b$Institut des Sciences Chimiques de Rennes(ISCR), UMR 6226 CNRS-Université de Rennes 1
Campus de Beaulieu, 35042 RENNES Cedex, France,

E-mail: didier.fasquelle@univ-littoral.fr

Abstract. Developing instrumentation systems compatible with the European RoHS directive (restriction of hazardous substances) to monitor our environment is of great interest for our society. Our research therefore aims at developing innovating integrated systems of detection dedicated to the characterization of various environmental exposures. These systems, which integrate new gas sensors containing lead-free oxides, are dedicated to the detection of flammable and toxic gases. We have firstly chosen to study semiconductor gas sensors implemented with lead-free oxides in view to develop RoHS devices. Therefore thick films deposited by spin-coating and screen-printing have been chosen for their robustness, ease to realize and ease to finally obtain cost-effective sensors. As crystalline defects and ionic vacancies are of great interest for gas detection, we have decided to study a non-stoichiometric composition of the BaSrTiFeO$_3$ sensible oxide. Non-stoichiometric BaSrTiFeO$_3$ lead-free oxide thick films were deposited by screen-printing on polycrystalline A1$_2$O$_3$ substrates covered by a layer of Ag-Pd acting as bottom electrode. The physical characterizations have revealed a crystalline structure mainly composed of BaTiO$_3$ pseudo-cubic phase and Ba$_4$Ti$_{12}$O$_{27}$ monoclinic phase for the powder, and a porous microstructure for the thick films. When compared to a BSTF thick film with a stoichiometric composition, a notable increase in the BSTF dielectric constant value was observed when taking into account of a similar microstructure and grain size. The loss tangent mean value varies more softly for the non-stoichiometric BaSrTiFeO$_3$ films than for the perovskite BSTF film as tan\(\delta\) decreases from 0.45 to 0.04 when the frequency increases from 100 Hz to 1 MHz.

1. Introduction

Functional oxides have been intensively studying by the scientific community since the 1990s. They present a wide range of interesting functionalities, such as high dielectric permittivity, piezoelectricity, pyroelectricity and ferroelectricity which have been largely developed in applications such as ceramic capacitors, tunable devices, actuators and sonars, I-R sensors and ferroelectric memories, respectively [1,2]. More recently, the community attention has been attracted by other properties and materials such as high temperature superconductivity, colossal magneto-resistance, multiferroics, gas sensing, half-metallic behaviour, thermoellectrics and oxides for fuel cells. The extended spectrum of involved materials has triggered extensive studies to understand the fundamental nature of existing systems, and then to modify and control novel materials for applications. These materials are characterized by strong interactions between the fundamental degrees of electron freedom (electron spin), charge,
orbital and their interplay with the lattice [3]. All oxides exhibit various crystalline structure. One of the best-known family is oxides that exhibit phase transitions in strongly correlated electron systems. A typical example is an oxide with a perovskite-type crystal structure (ABO$_3$). In these crystalline structures, the grain boundaries, impurities and structural defects strongly influence the dynamics of ferroelectric or ferroic domains, if the material is not in the paraelectric state. And when other phenomena occur like the catalytic activity, often relied on atomic scale defects such as oxygen vacancies, new defects can be generated. So in the same time the dynamics of defects are strongly influenced by local electric fields, domain boundaries, surfaces chemical potentials which are themselves influenced by ferroelectric or ferroic properties and catalytic action.

Today, gas detection on the industrial market mainly uses optical sensors, electro-chemical sensors often containing lead, and catalytic sensors based on platinum. Many commercial gas sensors are composed of electrochemical cells, especially those used in the detection of flammable gas. Industrial firms producing these lead-based sensors can consume more than a ton of lead per year. This is a concern because lead is one of the most hazardous and polluting raw materials; it affects the central nervous system and has the potential to induce infertility and cancer. In 2008, the modified European Restriction of Hazardous Substances (RoHS) directive appeared, prohibiting the use of hazardous substances like lead, cadmium and mercury. As such, there is an urgent need for lead-free components in Europe, and industry is now trying to produce electronic components and devices which comply with RoHS standards. In this frame, developing innovating gas sensors containing lead-free oxides and dedicated to the detection of hazardous substances is highly encouraged by authorities. Among the different technologies that can be used for the detection of dangerous toxic and flammable gases in industrial sites, as well as for monitoring indoor air quality in houses and public buildings, oxides have been implemented to realize gas sensors, and especially semi conductive gas sensors [4, 5]. In this kind of sensor, the material of the oxidation-reduction is not a metal, as is the case for a catalytic detector, but generally a semi-conductor metallic oxide with n or p-type behavior, like the well-known SnO$_2$ or ZnO, and whose conduction is due to oxygen vacancies (oxide not exactly stoichiometric). The redox reactions, or simply adsorption to the surface, will change the resistivity of the material, by varying the number of charge carriers. The material is heated, as in the case of the catalyst beads, but the measurement is different: it is the variation of the resistance of the material itself which is measured, and not that of the heating element. The measuring range of these devices depends on the implemented signal processing: either the range 0-100% LLE (Low Limit of Explosivity) or the range 0-100% V / V, either the range ppm. Like the catalytic technology, the semiconductor detectors are not selective and their sensitivity to various compounds will depend on the gas calibration. They require the presence of oxygen to function. Indeed, the presence of oxygen in the background determines a higher baseline resistance (formation of ionosorbed oxygen), and generally increases the response and recovery times. The semiconductor detectors for detecting flammable gases are not very used in the industry, as they age (due to heating) and thus derive very rapidly (within weeks for some). In addition, these detectors are influenced by ambient conditions, particularly by moisture. The water vapor adsorbs onto the surface of the semiconductor: this is an interfering problematic. The response time of these devices is very variable, from a few tens of seconds to several minutes. The lifetime of the sensors is of the order of several weeks to several years, depending on the context of use. Therefore, the use of solid-state detectors for the detection of flammable gas is not recommended. In opposition to this point, semiconductor oxides can be used for the detection of toxic gases and vapors.

In fact, gas detectors need to be implemented for monitoring the risk of poisoning caused by the possible presence of toxic gases or vapors, or for the protection of persons by monitoring the risk of suffocation from a lack of oxygen (anoxia) in confined premises and caused by gas leaks such as nitrogen (N2), helium (He). Modern technologies offer high performance in terms of compensation (humidity and / or temperature) and provide long-term stability. To meet different needs, three sensor technologies are currently met in this case: electrochemistry, semiconductor and optical devices. We
have firstly chosen to study semiconductor gas sensors implemented with lead-free oxides in view to develop RoHS devices. Therefore thick films deposited by spin-coating and screen-printing have been chosen for their robustness, ease to realize and ease to finally obtain cost-effective sensors. Our previous work enabled us to optimize the conditions of deposition of lead-free thick and thin films (BaTiO$_3$, BaSrTiO$_3$, BaTiSnO$_3$, BaSrTiFeO$_3$, SBN, KTN, ZnO and TiO$_2$) integrated to semiconductor gas sensors [4,5].

Among these sensors embedding a lead-free film based on a stoichiometric oxide, some materials have attracted our attention in view to study another possibility: As crystalline defects an ionic vacancies are of great interest for gas detection, i.e. for gas adsorption - desorption, a new emerging question appears: will this phenomenon be emphasized by a non-stoichiometric composition of the sensible oxide? So we have started works on a non-stoichiometric BaSrTiFeO$_3$ material. We present here a complete study of non-stoichiometric BaSrTiFeO$_3$ lead-free oxide thick films deposited on polycrystalline Al$_2$O$_3$ substrates, dedicated to the development of semiconductor gas sensors.

2 Experimental procedure

2.1 Preparation of BaSrTiFeO$_3$ powder

The composition Ba$_{0.85}$Sr$_{0.15}$Ti$_{0.9}$Fe$_{0.1}$O$_3$ was prepared by solid-state reaction, using amounts of BaO (ACROS ORGANICS, 90%), SrO (Alfa Aesar, 97%), TiO$_2$ (ACROS ORGANICS, 98%), and Fe$_2$O$_3$ (STREM CHEMICALS, 99.8%) oxides, with no respect of the required amount of oxygen in aim to make a non-stoichiometry in oxygen. The obtained BSTF precursor was mixed with alcohol in ball mill for 3h. The homogenized powder was dried at 300 °C for 6 h. and then calcined at 1100 °C for 3 h. The samples made with this powder were labeled BSTF-NS1. A second step of milling was done for 3h in order to decrease the grain size. The samples made with this double-milled powder were labeled BSTF-NS2.

2.2 Ink preparation

To formulate the thick-film ink, BSTF powder was combined with an organic vehicle (alpha-terpineol (ACROS ORGANICS, 97%), polyvinyl butyral (ACROS ORGANICS, Butvar B-98), 2-(2-butoxyethoxy)-ethyl acetate (Alfa Aesar, 98%) and polyethylene glycol (ACROS ORGANICS, M.W. 400) using a 60:40 ratio. The ink was milled by a roller to obtain a good homogeneity.

2.3 Film preparation and characterizations

High purity alumina substrates were coated by a silver-palladium ink (Ag-Pd, Tanaka Kikinzoku Kogyo K.K.) to realize the bottom electrode and then heated at 850 °C for 1 h to densify the Ag-Pd layer. For the electrical characterizations, BSTF thick films were deposited by screen-printing on Ag-Pd/Al$_2$O$_3$ substrates, and then sintered at 1100 °C for 2 h. Gold (Neyco, 99.99 %) / Chromium (CERAC, 99.99 %) (Au/Cr) upper electrodes were deposited by thermal evaporation. The obtained films presented a thickness ranging from 20 to 40 µm. For X-ray diffraction (XRD) analysis, a D8 Advance Bruker AXS (θ-2θ configuration) equipped with a monochromatized CuK$_\alpha$ radiation source was used. Surface morphology and thickness were determined by field-emission scanning electron microscopy (FE-SEM), using a JEOL JSM 6310F system working at a low accelerating voltage (5 kV). The resistance and capacitance parameters of BSTF films were investigated and measured by a HP4284A impedance analyzer using a metal-insulator-metal (MIM) structure. These parameters were used for calculating the dielectric constant ($\varepsilon'$), loss tangent (tanδ).

3. Results and discussion

Figure 1 shows the polycrystalline structure of the non-stoichiometric BSTF powder. This structure is mainly a combination of BaTiO$_3$ pseudo-cubic phase and Ba$_4$Ti$_{12}$O$_{27}$ monoclinic phase, given as references for identification (JCPDS files).
Figure 1. XRD pattern of non-stoichiometric BSTF thick film. (1) identifies the BaTiO$_3$ phase, (2) identifies the Ba$_4$Ti$_{12}$O$_{27}$ phase.

Figure 2 shows the organization of the crystalline cells of the main phases: a) the perovskite structure of BT in cubic phase, b) the monoclinic phase of Ba$_4$Ti$_{12}$O$_{27}$. Details on the different cells are given in Figure 2.

Figure 3 shows the microstructure of the two thick films deposited by screen printing on Ag-Pd/Al$_2$O$_3$ substrates, where the top and cross section views are given from the observation by FE-SEM. The film made with the powder only milled one time was labeled BSTF-NS1, while the powder with 2 milling steps was used to elaborate the film labeled BSTF-NS2. The film thickness, which was measured by observing the cross-section, was of about 30 µm for the BSTF-NS1 sample and of about 20 µm for the BSTF-NS2 sample. The grain size of the BSTF layers is rather regular with agglomerated grains. Although, it can be noticed that the film is porous as a binder was used in the ink preparation. All this binder was burnt during the sintering step and all organics were removed from the ink layer, creating holes in the film. This porous structure is of interest for gas sensing as the detection process can in this case involve the whole volume of the oxide layer, i.e. not only be linked to a surface reaction like in a dense thin film. The grain size ranged from 300 to 400 nm for BSTF-NS1 and from 100 to 150 nm for BSTF-NS2. The observation of the cross-section views clearly identifies the strong adhesion of BSTF/Ag-Pd layers on Al2O3 substrates.
Figure 3 FE-SEM photos of BSTF thick films. Images on left are for BSTF-NS1 and on right for BSTF-NS2. Top and cross-section views are given.

The dielectric characterizations were made on a metal-insulator-metal (MIM) structure. Figure 4 shows the frequency dependence of the dielectric constant ($\varepsilon'$) of the BSTF films where the frequency ranges from 100 Hz to 1 MHz at room temperature. As many dots, i.e. upper electrodes, were deposited on the samples, different curves are plotted in Figure 4. The $\varepsilon'$ mean values at 1 kHz and 100 kHz for BSTF-NS1 were 125 and 100, respectively; for BSTF-NS2, 68 and 58, respectively. The dielectric constant values of the BSTF-NS2 thick film are lower because of the lower grain size of this film, due to the use of a second step of powder milling. This effect of the grain size on the dielectric properties is well-known for ceramics and films [6,7,8,9]. When compared to a BSTF thick film with a stoichiometric composition [10], a notable increase in the BSTF dielectric constant value was observed when taking into account of a similar microstructure and grain size, i.e. by comparing with BSTF-NS1. A similar value of $\varepsilon'$, i.e. lower than 100 at room temperature has been measured on BSTF-NS2. On BSTF ceramics, dielectric constant values lower than 100 are observed as well [11]. All dielectric values are summarized in table 1.

Figure 4 Frequency dependence of the dielectric constant ($\varepsilon'$) given for the BSTF-NS1 (on left) and BSTF-NS2 thick films.
Table 1: Dielectric values given for the BSTF-NS1 and BSTF-NS2. Values measured on a stoichiometric composition of BSTF are given as well for comparison [10].

| Frequency | Dielectric constant (mean value) | Loss tangent (mean value) |
|-----------|--------------------------------|--------------------------|
|           | 1 kHz                         | 100 kHz                  |
| BSTF-NS1  | 125                           | 100                      |
| BSTF-NS2  | 68                            | 58                       |
| BSTF [10]| 65                            | 52                       |

The frequency dependence of the loss tangent (tanδ) at room temperature is shown in Figure 5. In our frequency range, the loss tangent variation is quite similar for the 2 films. As many upper electrodes were deposited on the samples, different curves are plotted in Figure 5. The loss tangent mean value varies more softly for the non-stoichiometric BaSrTiFeO₃ films than for the perovskite BSTF film [10]. In fact tanδ decreases here from 0.45 to 0.04 when the frequency increases from 100 Hz to 1 MHz.

About the important decrease of the ε’ and tanδ evolutions in function of the frequency, it is interesting to remind that our thick films are very porous due to the relatively low percentage of oxide powder in our inks, i.e. 60% for BSTF films. A high porosity in a film implies that the layer is composed of grains and holes, where the holes are filled with air. This porous structure is therefore in relation with the observed evolutions. But the porosity is not problematic as it is really a desired characteristic of the microstructure because we dedicate these porous thick films to semiconductor gas sensors, and in this case the porosity is of importance for the adsorption-desorption process.

Figure 5 Frequency dependence of the loss tangent (tanδ) for the BSTF-NS1 (on left) and BSTF-NS2 thick films.

4. Conclusion
Ba₀.₈₅Sr₀.₁₅Ti₀.₉Fe₀.₁O₃ powder, with a non-stoichiometry in oxygen, has been synthesized by solid-state reaction. BSTF inks were prepared and deposited on Ag-Pd/Al₂O₃ substrates by screen printing to obtain porous thick films dedicated to lead-free gas sensors for RoHS devices. The physical characterizations have revealed a crystalline structure mainly composed of BaTiO₃ pseudo-cubic phase and Ba₅Ti₁₂O₂₇ monoclinic phase for the powder, and a porous microstructure for the thick films. These porous polycrystalline films have given significant differences in dielectric properties when compared to a perovskite BSTF thick film.

Acknowledgment
The SEM photos were made by Dr Lucie Courcot from the Maison de la Recherche en Environnement Naturel (MREN), Université du Littoral Côte d’Opale.
References
[1] Jaffe B, Cook WR and Jaffe H, 1971, Piezoelectric Ceramics, Academic Press London and New York.
[2] Scott J F, 2007, Science 315, 954.
[3] Ramesh R, 2013, Current Science, Vol. 105, No. 8, pp 1107-1114.
[4] Fasquelle D, Députier S, Mascot M, Uschanoff N, Bouquet V, Demange V, Guilloux-Viry M, Carru J.-C. 2013, Advanced Materials Research Vol. 789, pp 105-111.
[5] Fasquelle D, 2014 International Innovation, pp 106-108.
[6] Luan W, Gao L, and Guo J, 1999, Ceramics International 25 pp.727-729.
[7] Tusseau-Nenez S, Ganne J.-P., Maglione M, Morell A, Niepce J.-C., Paté M., 2004, Journal of The European Ceramic Society 24 pp. 3003–3011.
[8] Fasquelle D, Mascot M, and Carru JC, 2011, Advanced Materials Research Vol. 277, pp 1-10.
[9] Fasquelle D, Mascot M, and Carru JC, 2012, Solid-State Electronics 75 pp. 6–12.
[10] El Romeh MA, Fasquelle D, Députier S, Mascot M, and Guilloux-Viry M, 2016, Journal of Materials Science: Materials in Electronics, Vol. 27, Issue 2, pp 2096–2102.
[11] Guo Z, Pan L, Bi C, Qiu H, Zhao X, Yang L, and Rafique MY, 2013, Journal of Magnetism and Magnetic Materials, 325, pp. 24-28.