



## Resistive switching in ceramic multiferroic $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$

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### ABSTRACT

We report resistive switching effects in polycrystalline samples of the multiferroic  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  with silver electrodes. Mössbauer spectroscopy shows that upon Ca-doping the Fe remains in a  $3+$  valence state, suggesting charge compensation through the creation of large amounts of oxygen vacancies. Electrical characterization shows that the oxide/metal resistance can be switched between high and low resistance states by applying voltage pulses. This process was shown to be forming free and a strong relaxation after switching was found. We rationalize our results by considering oxygen vacancies migration to and from the metal–oxide interface, resulting in variations of the Schottky potential barrier height that modulate the interface resistance.

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### 1. Introduction

Resistive switching (RS) [1,2] is defined as the reversible and non-volatile change of the resistance of a material under the application of electrical pulses. RS in transition metal oxides has been observed in many binary and complex compounds, being the basis for the development of novel non-volatile resistance random access memories (RRAM). The typical RS system consists of a capacitor-like structure, where an insulating or semiconducting material is sandwiched between metallic electrodes. In the case of complex oxides, the RS effect is interface-related, that is, it takes place at the interface between a metal electrode and the oxide, playing a key role in the presence of oxygen vacancies (which can be moved by the action of the electrical field during pulsing) that modulate the interface resistance.

Bismuth ferrite ( $\text{BiFeO}_3$ ) is a room temperature multiferroic [3]; it is ferroelectric with  $T_C \sim 1140$  K, and antiferromagnetic with  $T_N \sim 640$  K. In addition to multiferroicity,  $\text{BiFeO}_3$  has been shown to display RS properties in thin film form [4–6]. Here we show for the first time in ceramic samples that an accumulative, forming free, RS effect can be observed in Ca-doped  $\text{BiFeO}_3$  with silver contacts. A strong relaxation effect is found after switching, indicating a high diffusivity of oxygen vacancies in the absence of electrical fields.

### 2. Experimental

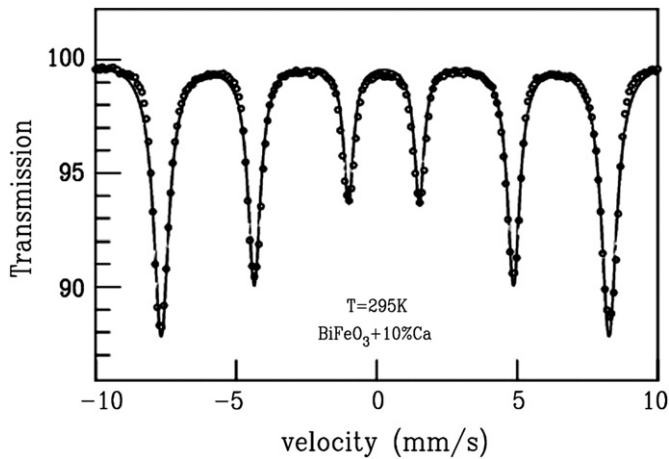
$\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  (BCFO) polycrystalline samples (powders and pellets) were prepared by means of the standard solid state reactions. Mössbauer spectra were recorded using a constant

acceleration drive spectrometer and a commercial  $^{57}\text{Co}$ :Rh gamma ray source. In order to perform electrical measurements,  $\sim 1$  mm<sup>2</sup> silver contacts were hand-painted ( $\sim 1$  mm of separation) with commercial silver paste and the sample was subsequently wired in a two-terminals configuration. We should stress that Ca-doping lowers the high resistance of  $\text{BiFeO}_3$  ( $> 1$  G $\Omega$ ) to measurable values ( $\sim 150$  M $\Omega$ ). Electrical pulses with a time width of  $\sim 1$  ms were injected at room temperature by a Keithley 2400 source meter. After pulsing, the two-terminal resistance was measured by the same instrument applying a voltage bias of 3 V.

### 3. Results and discussion

In BCFO, the charge balance upon substitution of trivalent  $\text{Bi}^{3+}$  with divalent  $\text{Ca}^{2+}$  could force the trivalent  $\text{Fe}^{3+}$  to change into a mixed  $\text{Fe}^{3+/4+}$  valence state or induce the appearance of oxygen vacancies. The latter is extremely important in the context of the RS effect provided the key role played by oxygen vacancies in the switching of metal–oxides interfaces [7]. In order to probe the Fe valence of the BCFO sample a  $^{57}\text{Fe}$  Mössbauer spectrum was recorded at room temperature. The material was enriched with 30% of the  $^{57}\text{Fe}$  isotope to ensure a good signal to noise ratio in a reasonable counting time. The spectrum is shown in Fig. 1. One observes a single 6-line spectrum characteristic of a magnetically ordered state of  $\text{Fe}^{3+}$  ions. The valence of Fe can be assessed both by the isomer shift value (0.39 mm/s) and by the large value of the hyperfine field (49.5 T), corresponding to a Fe moment of about 5  $\mu\text{B}$ . In agreement with the previous reports [8], no significant traces of  $\text{Fe}^{4+}$  are found in the spectrum, implying that charge balance upon Ca-doping takes place through the formation of oxygen vacancies. Fig. 2(a) shows the evolution of the BCFO resistance after the application of 200 V pulses with alternate polarities. A clear bipolar resistive switching effect is found, with a high resistance state of  $\sim 160$  M $\Omega$  and a low resistance

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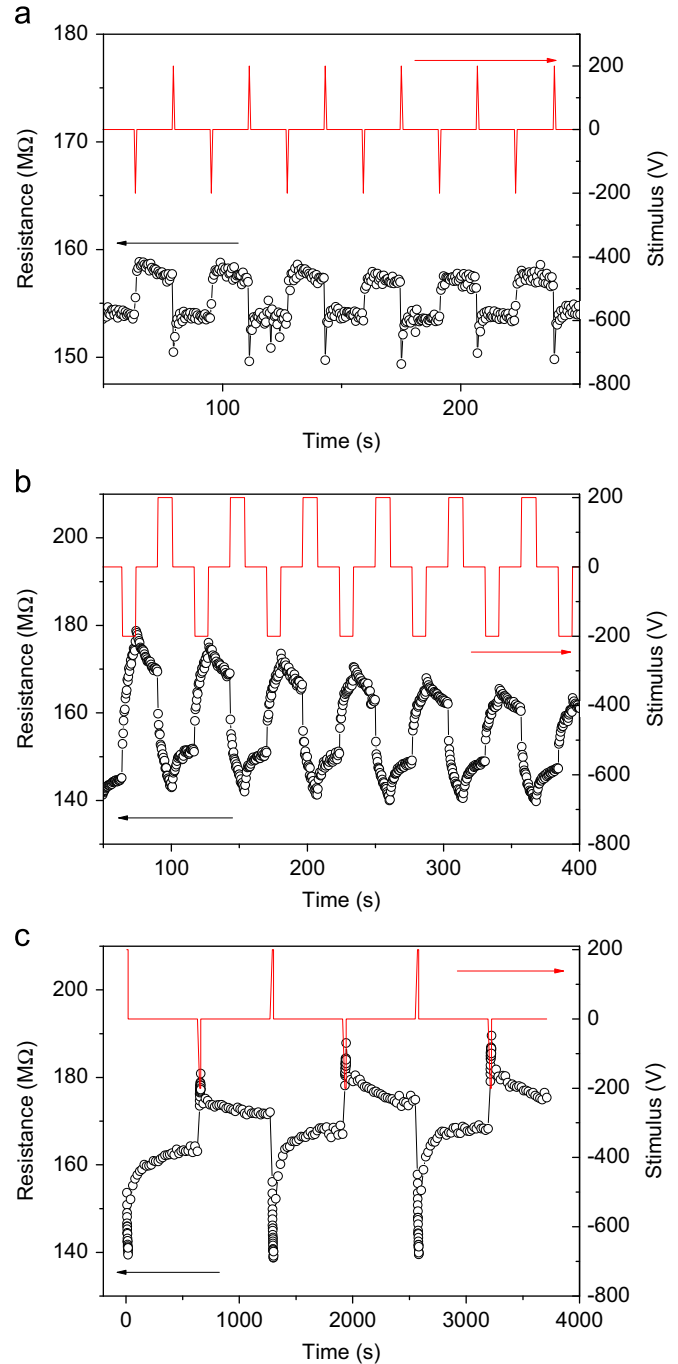


**Fig. 1.** Room temperature Mössbauer spectrum corresponding to a  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  sample.

state of  $\sim 150 \text{ M}\Omega$ . We checked that the observed RS is not an artefact related to a capacitive effect. We argue that the application of electrical pulses induces oxygen vacancies migration through the oxide, and, in particular, modifies the oxygen vacancies profile close to the metal–insulator interface [8], changing its resistance. For instance, a negative voltage applied to an Ag electrode induces the migration of positively charged oxygen vacancies through the BCFO to the metal–oxide interface. These vacancies accumulate close to the interface, resulting in a lowering of the Schottky potential barrier [1] and in a low resistance state. The application of an opposite voltage induces the movement of oxygen vacancies from the interface to the BCFO bulk, increasing the Schottky potential barrier and resulting in a high resistance state. We can quantify the RS effect by defining

$$\text{RS (\%)} = (R_{\text{high}} - R_{\text{low}}) / R_{\text{av}}$$

where  $R_{\text{high}}$  and  $R_{\text{low}}$  are the high and low resistance values, respectively, and  $R_{\text{av}}$  is the average between  $R_{\text{high}}$  and  $R_{\text{low}}$ . Using this definition, the RS value observed after pulsing with 200 V pulses is  $\sim 6\%$ . This figure is lower than that found in BCFO thin films ( $\sim 200\%$ ) [6], which is arguably related to the low electrical fields (and therefore relatively low oxygen vacancies drift) achievable during pulsing in ceramic samples with metallic electrodes separated by distances of millimeters. On the contrary, in the case of thin films the electrodes can be separated by tens of nanometers and therefore the electrical fields can be several orders of magnitude higher, leading to an increased drift of oxygen vacancies. Interestingly, we have found that the BCFO starts to switch immediately after pulsing, without any previous forming process. This should be related to the high concentration of oxygen vacancies present in our BCFO sample that facilitates the resistive switching behavior. In order to test the effect of accumulation of pulses, we have repeated the previous experiment by pulsing with trains of 25 pulses of  $\pm 200 \text{ V}$ , followed by trains of 25 pulses of the same voltage but with opposite polarity, as shown in Fig. 2(b). It is found that the RS immediately after pulsing increases to about 19%, indicating that the RS effect is accumulative. An interesting feature that can be observed from Fig. 2(b) is the existence of relaxation processes both for the high and low resistance states. Indeed, 15 s after pulsing both  $R_{\text{high}}$  and  $R_{\text{low}}$  relax towards their average value [9] and RS falls to  $\sim 11\%$ . Ten minutes after pulsing with 25 pulses of  $\pm 200 \text{ V}$ , relaxation continues and RS is of about  $\sim 5\%$ , as can be observed from Fig. 2(c). This indicates that the resistive switching effect presents some degree of volatility, related to oxygen vacancies diffusion in the absence of an electrical field; similar results were reported in BFO thin films by Yin et al. [5], with typical relaxation times of the order of tens of minutes, which is consistent with our results. Further experiments exploring the resistive



**Fig. 2.** (a) Room temperature resistance vs. time for a  $\text{Bi}_{0.9}\text{Ca}_{0.1}\text{FeO}_3$  sample pulsed with  $\pm 200 \text{ V}$  single pulses. (b) Idem in (a) with trains of 25 pulses of  $\pm 200 \text{ V}$ . The waiting time between two consecutive trains of pulses is of about 15 s. (c) Idem in (b), with a longer waiting time ( $\sim 10 \text{ min}$ ) between two consecutive trains of pulses.

switching mechanism in BCFO with different metallic electrodes (Ag, Ti, Al, Pt) are under way.

#### 4. Conclusions

In summary, we have shown the existence of RS in ceramic samples of Ca-doped bismuth ferrite with Ag electrodes. We have shown by means of Mössbauer spectroscopy that Fe in BCFO remains in a trivalent state upon Ca-doping, inferring the presence of oxygen vacancies due to charge compensation. The observed switching was

found to be forming free and accumulative with the number of pulses. It was observed that both the high and low resistance states relax with time. We qualitatively explain our results by considering oxygen vacancies migration to and from the metal–oxide interface, resulting in variations of the Schottky potential barrier height that modulate the interface resistance.

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- [9] The relaxation of  $R_{\text{high}}$  to lower resistance values and  $R_{\text{low}}$  to higher resistance values shows that the accumulation effect is not an artefact related to self-heating; in that case, the relaxation of  $R_{\text{high}}$  and  $R_{\text{low}}$  should present the *same* trend.