Electronic Supplementary Information (ESI)

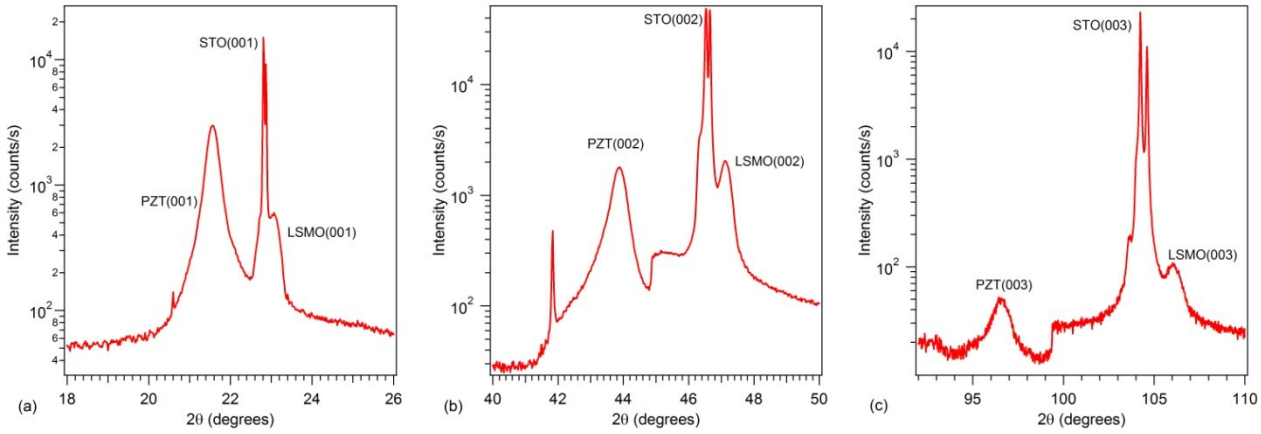
Polarization landscape effects in electron-induced surface chemical decomposition of (001) lead zirco-titanate, evidenced by Pb 5d photoelectron spectromicroscopy

Laura E. Abramiuc[1,2], Liviu C. Tănase[1,2], Alexei Barinov[3], Nicoleta G. Apostol[1], Cristina Chirilă[1], Lucian Trupină[1], Lucian Pintilie[1], Cristian M. Teodorescu[1]*

[1]National Institute of Materials Physics, Atomiștilor 405A, 077125 Măgurele – Ilfov, Romania
[2]University of Bucharest, Faculty of Physics, Atomiștilor 405, 077125 Măgurele – Ilfov, Romania
[3]Elettra Sincrotrone Trieste, S.S. 14 - km 163,5, Area Science Park, 34169 Basovizza – Trieste, Italy

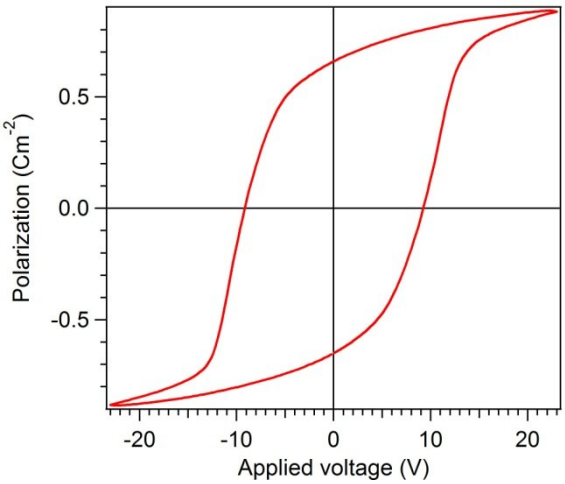
1. X-ray diffraction

Measurements performed in Bragg-Brentano geometry using a Bruker D8 Advance diffractometer, X-rays produced by a Cu anode (Cu K_α wavelength λ =), nickel filter for attenuating Cu K_β radiation.



2. *P*(*E*) hysteresis loops

The hysteresis measurements were performed at room temperature, using a ferritester TF2000 (AixACCT). The Au top electrodes with 0.01 mm ^{2} area were deposited thought a shadow mask by RF magnetron sputtering.



3. Inelastic mean free path effects in stoichiometry derivations

Owing to inelastic mean free path (IMFP)effects (S. Hüfner, *Photoelectron Spectroscopy: Principles and Applications*, Springer, 2003) the apparent stoichiometry deviates from the ideal one. For instance, in the case of PbO termination, the film is constituted by successive layers such as: PbO / $(Ti,Zr)O_2$ / PbO / $(Ti,Zr)O_2$ / PbO / ..., spaced by c / 2, where c is the [001] PZT lattice constant (~ 4.1 Å). Owing to inelastic mean free path effects which are manifested by different escape depths λ_{Pb}, λ_{Ti}, λ_{Zr}, the atomic concentrations of each element X measured by XPS, c_X, related to the 'ideal' ones $c_X^{(0)}$ are connected by the following equations:

$$c_{Pb} = c_{Pb}^{(0)} \sum_{j=0}^{\infty} \exp\left(-\frac{jc}{\lambda_{Pb}}\right) = \frac{c_{Pb}^{(0)}}{1-\exp\left(-\frac{c}{\lambda_{Pb}}\right)} \qquad \text{(ESI-1)}$$

$$c_{Ti,Zr} = c_{Ti,Zr}^{(0)} \sum_{j=0}^{\infty} \exp\left(-\frac{(2j+1)c}{2\lambda_{Ti,Zr}}\right) = \frac{c_{Ti,Zr}^{(0)} \exp\left(-\frac{c}{2\lambda_{Ti,Zr}}\right)}{1-\exp\left(-\frac{c}{\lambda_{Ti,Zr}}\right)} \qquad \text{(ESI-2)}$$

Similar formulas may be written also for (Zr, Ti)O_2 terminations.
Thus, the observed [Pb]/[Zr + Ti] ratio deviates from unity even for a perfectly stoichiometric sample, being given by:

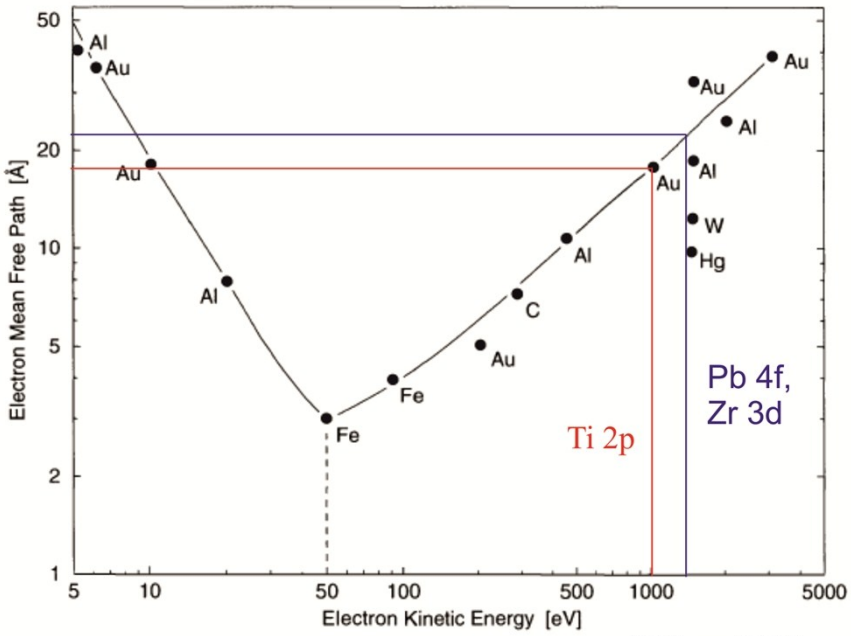
$$\frac{\left\{1-\exp\left(-\frac{c}{\lambda_{Ti}}\right)\right\}\left\{1-\exp\left(-\frac{c}{\lambda_{Zr}}\right)\right\}}{\left\{1-\exp\left(-\frac{c}{\lambda_{Pb}}\right)\right\}\left\{(1-x)\exp\left(-\frac{c}{2\lambda_{Ti}}\right)\left[1-\exp\left(-\frac{c}{\lambda_{Zr}}\right)\right]+x\exp\left(-\frac{c}{2\lambda_{Ti,Zr}}\right)\left[1-\exp\left(-\frac{c}{\lambda_{Ti}}\right)\right]\right\}} \qquad \text{(ESI-3)}$$

for PbO termination and by

$$\frac{\exp\left(-\frac{c}{2\lambda_{Pb}}\right)\left\{1-\exp\left(-\frac{c}{\lambda_{Ti}}\right)\right\}\left\{1-\exp\left(-\frac{c}{\lambda_{Zr}}\right)\right\}}{\left\{1-\exp\left(-\frac{c}{\lambda_{Pb}}\right)\right\}\left\{(1-x)\left[1-\exp\left(-\frac{c}{\lambda_{Zr}}\right)\right]+x\left[1-\exp\left(-\frac{c}{\lambda_{Ti}}\right)\right]\right\}} \qquad \text{(ESI-4)}$$

for (Zr, Ti)O_2 termination, x being the Zr content per formula unit.

There are known uncertainities regarding the “universal curve” of the IMFP. For instance, below we reproduce the IMFP from the above Reference (Hüfner, 2003) together with lines representing Pb 4f, Zr 3d and Ti 2p.



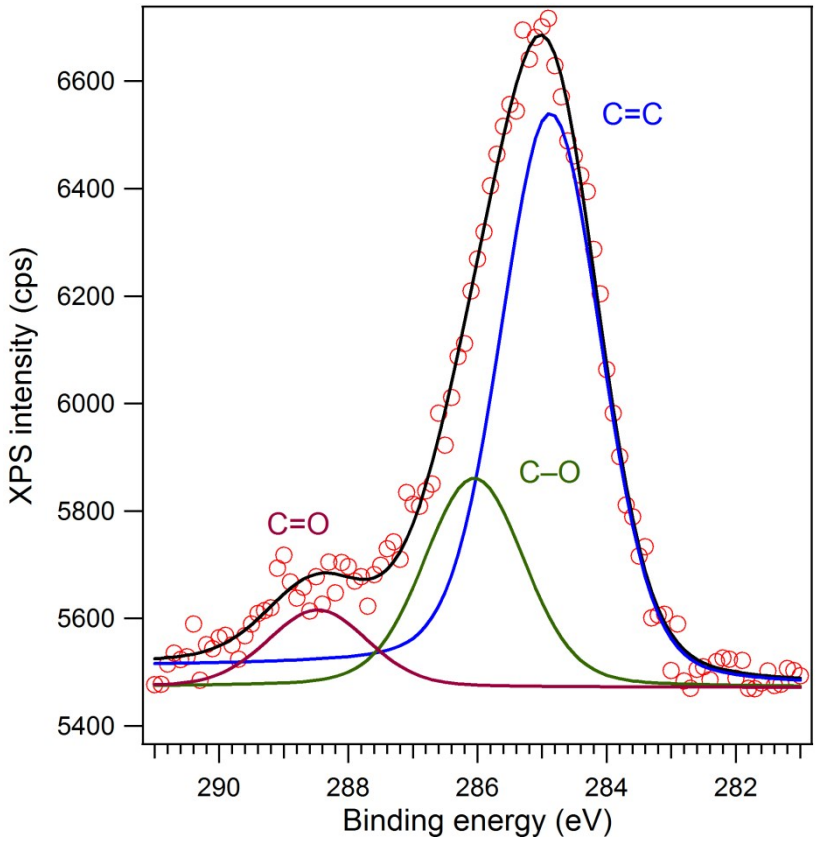
Hüfner, 2003

The obtained values are in good agreement with the empirical formula of Seah and Dench (M. P. Seah and W. A. Dench, *Surf. Interf. Anal.*, 1979, **1**, 2–11) for elements:

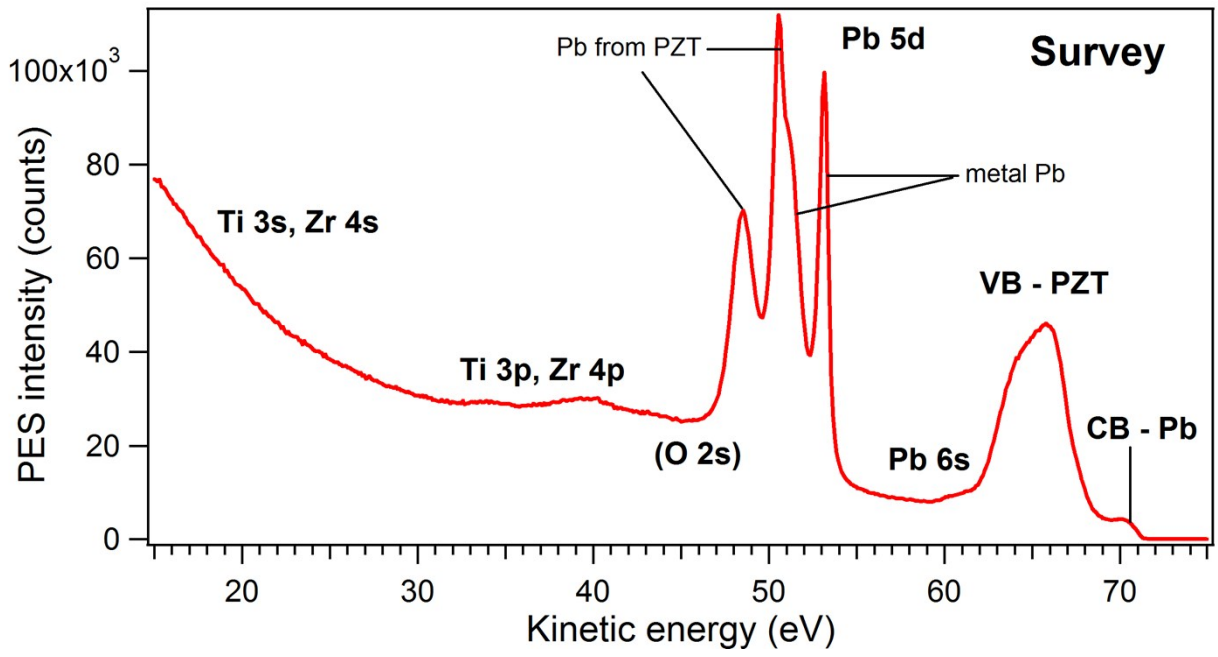
$$\lambda[\mathrm{nm}] \approx \frac{143}{KE[\mathrm{eV}]^2} + 0.054\sqrt{KE[\mathrm{eV}]} \qquad \text{(ESI-5)}$$

One obtains $\lambda \approx 20$ Å for Pb 4f, 19.5 Å for Zr 3d, and 17 Å for Ti 2p. For $x \approx 0.28$ (note that this observed value might also deviate) the obtained ratio is 1.25 for PbO termination and 1.01 for (Zr, Ti)O_2 termination. From the stoichiometry derived for $P^{(+)}$ areas [Pb]/[Zr + Ti] = 1.13, by a simple linear interpolation, one obtains an equal proportion of areas with PbO termination and (Zr, Ti)O_2 termination. For the $P^{(0)}$ areas, it seems that only 25 % of the surface is PbO terminated. But, owing to the uncertainities in the IMFP, we cannot speculate more on this aspect. For the purpose of our study, we must retain just the fact that a significant area of the film presents PbO termination and that deviations of the observed [Pb]/[Zr + Ti] ratio from unity may be attributed to IMFP effects.

4. C 1s XPS spectrum



5. Photoemission survey spectrum, with photon energy $h\nu = 74$ eV



6. Derivation of the Fermi level (E_F) position with respect to the conduction band minimum (E_{Cm})

Suppose one knows the position of the doping levels E_D in the bandgap and their atomic concentration N_D. One starts from the neutrality condition in a n-doped semiconductor:

$$N_C F_{1/2}\left(\frac{E_F - E_{Cm}}{k_B T}\right) = \frac{N_D}{1 + 2\exp\left(\frac{E_F - E_D}{k_B T}\right)} \tag{ESI-6}$$

The right hand side term is the electron concentration. N_C is the volume density of states in the conduction band:

$$N_C = \frac{\sqrt{2\pi m^* k_B T}}{h^3} \tag{ESI-7}$$

The left hand side represents the quantity of ionized donors, based on a Gibbs distribution. Each donor may accomodate two electronic states. $F_{1/2}(x)$ is the Fermi integral, defined as:

$$F_{\frac{1}{2}}(x) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{y^{1/2} dy}{1 + \exp(y - x)} \approx \begin{cases} \exp(x), for\ x < -2 \\ \frac{4}{3\sqrt{\pi}} x^{3/2}, for\ x > 5 \end{cases} \tag{ESI-8}$$

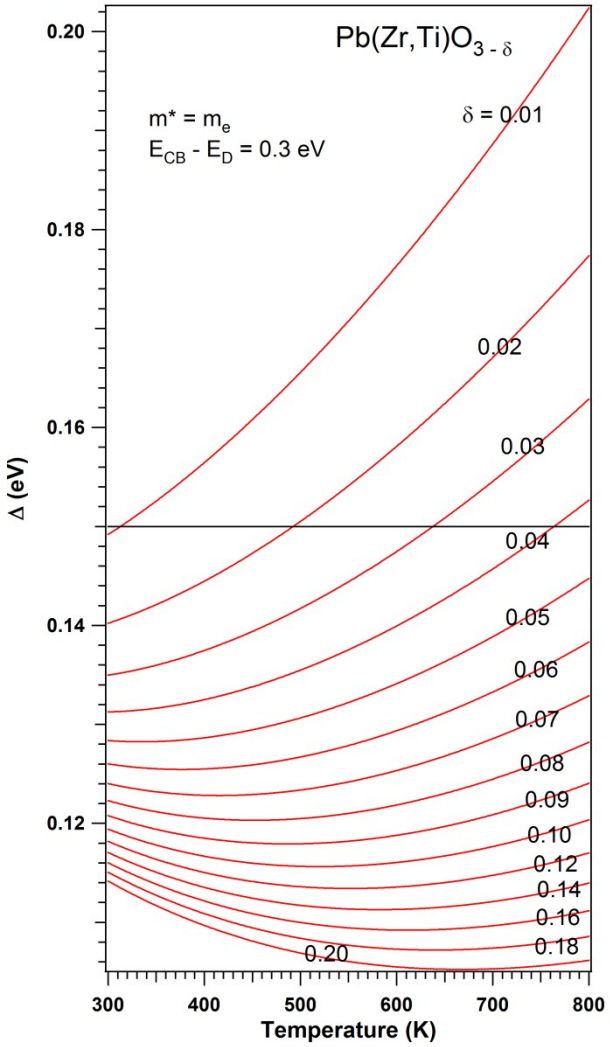
For $E_{Cm} - E_F > 2k_B T$, we may then write:

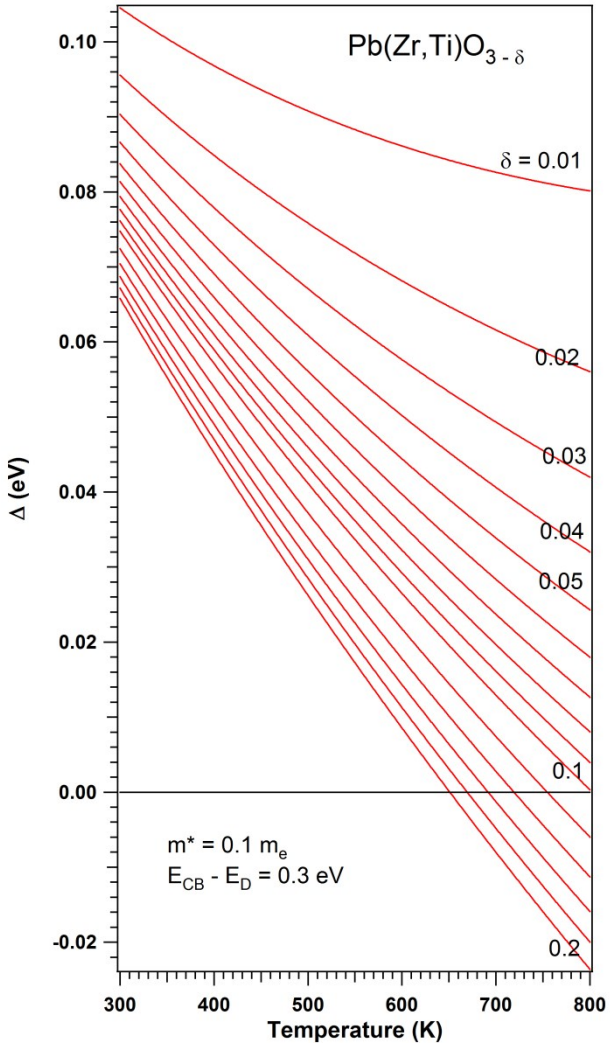
$$N_C \exp\left(\frac{E_F - E_{Cm}}{k_B T}\right) = \frac{N_D}{1 + 2\exp\left(\frac{E_F - E_D}{k_B T}\right)} \tag{ESI-9}$$

Solving this equation with respect to $\Delta \equiv E_{Cm} - E_F$ yields equation (10) from the main text of the article:

$$\Delta = k_B T \ln \frac{4\exp\left(\frac{E_{Cm} - E_D}{k_B T}\right)}{\sqrt{1 + \frac{8N_D}{N_C}\exp\left(\frac{E_{Cm} - E_D}{k_B T}\right)} - 1} \approx \frac{E_{Cm} - E_D}{2} + \frac{k_B T}{2} \ln \frac{2N_C(T)}{N_D} \tag{10} \equiv \text{(ESI-10)}$$

Apart for temperature, N_C depends also on the effective mass of the electron in the conduction band. Plots of Δ as function of temperature, for two different electronic masses, are represented in the figure below.


Pb(Zr,Ti)O3 - δ
m* = me
ECB - ED = 0.3 eV
δ = 0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.10
0.12
0.14
0.16
0.18
0.20
Δ (eV)
Temperature (K)


Pb(Zr,Ti)O3 - δ
δ = 0.01
0.02
0.03
0.04
0.05
0.1
0.2
m* = 0.1 me
ECB - ED = 0.3 eV
Δ (eV)
Temperature (K)