### [1]Supplementary information to

# Oxygen release technique as a method for the determination of «$\delta$ - $pO_2$ - $T$» diagrams for MIEC oxides.

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## [2]Results of characterization of SCF and SF samples by means of TG, TPD-$O_2$ and *in situ* high-temperature X-ray diffraction

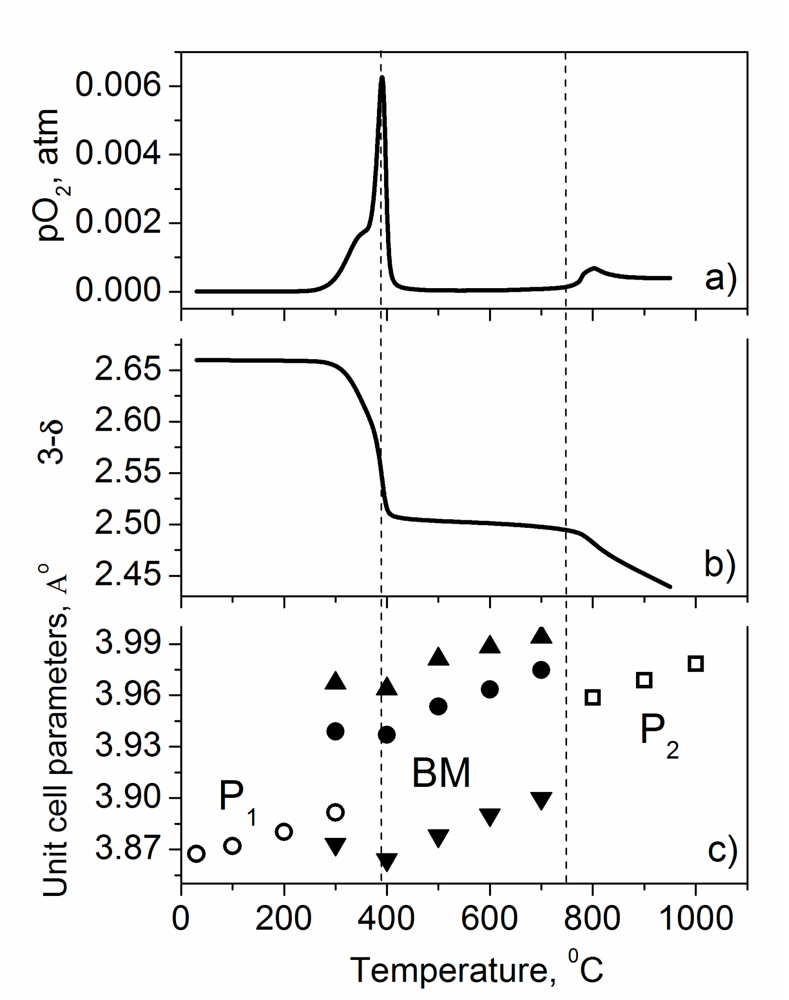

Fig. 1. Characterization of *SCF* powder sample (56-63 μm, m=1.00g); (a) – differential and (b) – integral forms of TPD-$O_2$ data (V = 1°/min, $F_{He}$ = 50 ml/min); (c) XRD – the dependence of the structural parameters on temperature. As can be seen from the fig. 1a, $pO_2$ at T~800°C does not exceed $10^{-3}$ atm.

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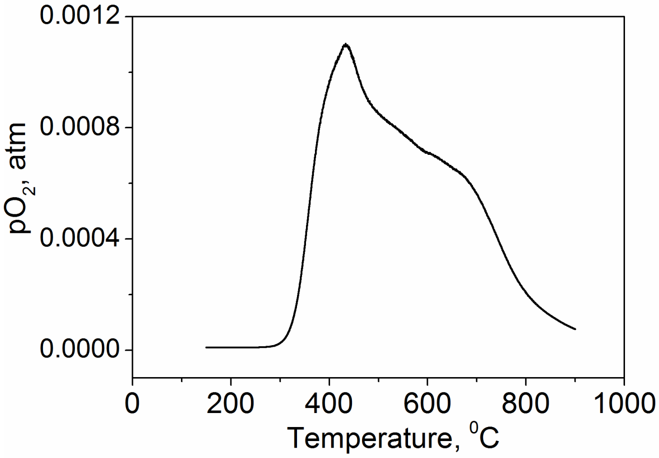

Fig.2. TPD-$O_2$ data for *SF* powder sample (56-63 μm, m=0.771g); V = 1°/min, $F_{He}$ = 50 ml/min

## [3]Quasi-equilibrium model of oxygen release from MIEC oxides

According to that the experimental dependence of the nonstoichiometry of the SCF oxide as function of $pO_2$ can be approximated by logarithmic law within temperature range of cubic perovskite phase [1, 2]

$$\delta = \delta_0 - b * \ln pO_2 / p \tag{1}$$

where *b* is the coefficient of proportionality,

$\delta_o$ is the equilibrium oxygen nonstoichiometry of the oxide at $pO_2=p$,

the dependence of oxygen pressure *versus* time during a slow helium blowing over the sample (compared to the rate of exchange of oxygen between the sample and the gas phase) can be determined as mass balance between of oxygen flow in, the rate of oxygen release from the sample and oxygen flow out of the reactor.

$$V_r \frac{p^*}{RT} \frac{dpO_2 / p}{dt} = J_{in} pO_{2in} / p - J_{out} pO_2 / p + \frac{dQ}{dt} \tag{2}$$

where

$$Q(t) = \frac{1}{2}(\delta(t) - \delta(0)) * W \tag{3}$$

is the quantity of released oxygen

If we neglect the oxygen partial pressure of the incoming stream and the additional oxygen stream from the sample e.g. $J_{in} = J_{out}$ then

$$V_r \frac{p^*}{RT} \frac{dpO_2 / p}{dt} = -J_{in} pO_2 / p - \frac{Wb}{2pO_2 / p} \frac{dpO_2 / p}{dt} \tag{4}$$

ignoring the accumulation of oxygen in small free reactor volume e.g. $V_r=0$ and using Eq.1 and Eq.2 we will get

$$\frac{dpO_2/p}{(pO_2/p)^2} = -J_{in}\frac{2}{Wb}dt \qquad (5)$$

After integrating (5)

$$pO_2/p = \frac{pO_{2,0}/p}{1+\frac{2J_{in}pO_{2,0}/p}{Wb}t} = \frac{pO_{2,0}/p}{1+\frac{t}{t_0}} \qquad (6)$$

where $pO_{2,0}$ is oxygen partial pressure near the sample at $t$=0, $t_0 = \frac{Wb}{2J_{in}pO_{2,0}/p}$ - is the characteristic time of oxygen release from the sample.

One can see in eq.6 that the dependence of oxygen partial pressure *vs.* time admits affine transformation along the time axis, which agrees with the experimentally established dependence $t^* = k \times t \times F_{He}/m$, since the mass of the sample is proportional to the quantity of oxide $W$ and $F_{He} = J_{in}\frac{RT}{p*}$, where $\frac{RT}{p*}$ is the volume of 1 mole of gas.

The rate of quasi-equilibrium oxygen release from the sample in a flow reactor is inversely proportional to time:

$$J_{O2} = J_{in}pO_2/p = \frac{J_{in}pO_{2,0}/p}{1+t/t_0} = \frac{Wb}{2}\frac{1}{t_0+t} = \frac{Q_0}{t_0+t} \qquad (7)$$

where $Q_0 = \frac{Wb}{2}$, and the amount of released oxygen is logarithmically dependent on time

$$Q_{O2} == Q_0\ln(t/t_0+1) \qquad (8)$$

Equations (7) and (8) can be rewritten in the form of so-called Elovich equations [3]:

$$\frac{dQ}{dt} = \frac{Q_0}{t_0}\exp(-\frac{Q}{Q_0}) \qquad (9)$$

It shows that the rate of oxygen release from the samples, providing the balance (eq. 5), exponentially decreases with decreasing oxygen content in the oxide. The described model is in good agreement with the experimental data (Fig. 3).

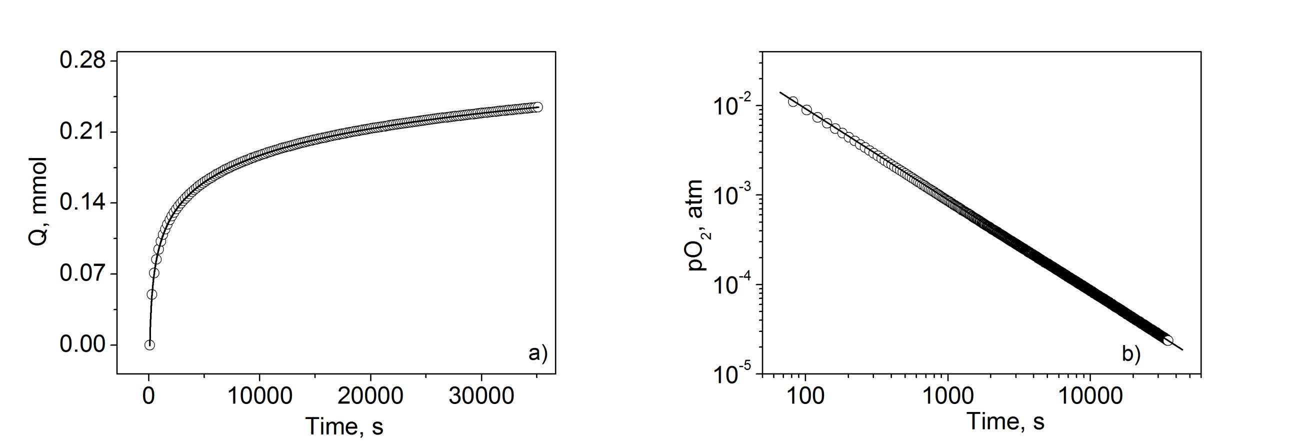

Fig. 3. (a) Oxygen released from the sample, and (b) Oxygen partial pressure as functions of the time at T=900°C. *SCF* powder (56-63μm, m=1.00g). Step-like change of the oxygen partial pressure at reactor inlet from 0.2 to $10^{-5}$ atm. *He* flow rate = 50 ml/min. Circles – experimental, solid lines – least square calculated data.

It should be noted that Elovich equation (eq. 9) is used in heterogeneous catalysis to describe adsorption/desorption on active centers with even inhomogeneous distribution of energy [3], and to describe the processes involving the changes of energy parameters [4, 5]. So, when the dependence of the equilibrium concentration of oxygen in the sample is proportional to $ln(pO_2/p)$, and oxygen release under the quasi-equilibrium conditions is described by Elovich equation (eq. 9) one may assume that oxygen release proceeds in the self-inhibiting mode because the energy barriers increase in the course of the process.

The quasi-equilibrium character of the release of oxygen from the samples of SCF, in the cubic perovskite phase of $P_1$, is associated with a high exchange rate of the oxide with the gas phase and the logarithmic dependence (eq. 1). On the one hand, small changes in the oxygen content in the sample (stoichiometry) cause a significant drop in the equilibrium oxygen pressure $P_e$. On the other hand, a rapid exchange of the gas phase with the sample and a decrease in the rate of oxygen removal from the reactor ($\sim F_{He}pO_2/p$), result in the convergence of equilibrium pressure $P_e$ and $pO_2$ in the reactor.

## References:

1. L.M. Liu, T.H. Lee, L. Qiu, Y.L. Yang and A.J. Jacobson, *Materials Research Bulletin*, 1996, **31**, 29.

2. N. Grunbaum, L. Mogni, F. Prado and A. Caneiro, *J. Solid State Chem.*, 2004, **177**, 2350

3. S.L. Kiperman, *Introduction in kinetics of heterogeneous catalytic reactions, "Nauka" Moscow*, 1964

4. P. Kofstad, *High – temperature oxidation of metals, John Willey and sons, inc. New York-London-Sydney*, 1966

5. J. Fleig, R. Mercle and J. Maier, *Physical Chemistry Chemical Physics,* 2007, **9**, 2713

## [4]Dependence $pO_2$ *vs.* time for SCF samples of different sizes

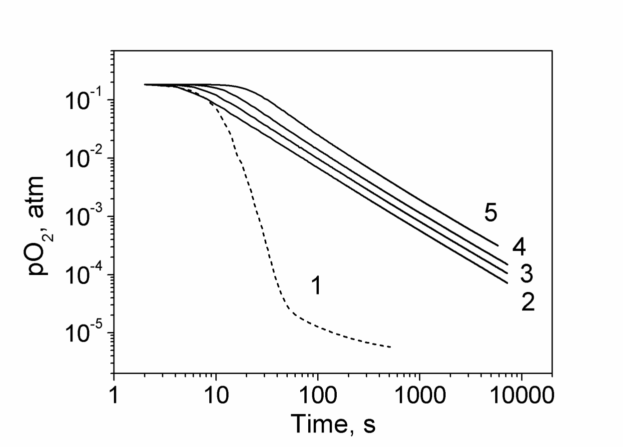

Fig. 4. Dependence of $pO_2$ *vs.* time for *SCF* sintered disk (d=15.5 mm; h=1.5 mm; m = 1.36 g) at 900°C, $F_{He}$ = 100 (2); 70 (3); 50 (4); 30 (5) ml/min. (1) –the change of $pO_2$ in the reactor without oxygen release, $F_{He}$ = 100 ml/min.

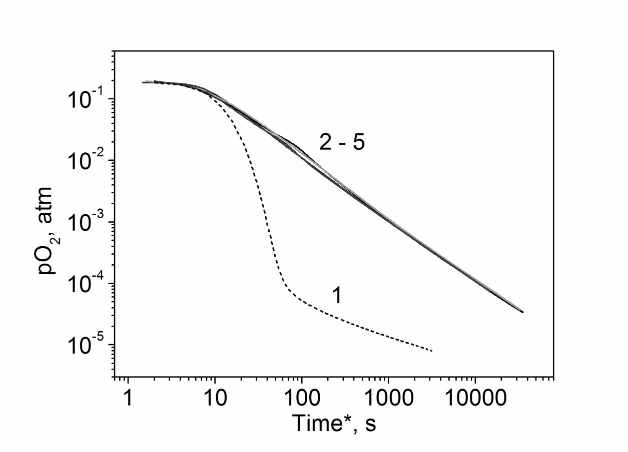

Fig. 5. Affine transformation $t^* \rightarrow t \times F_{He} / m$ of $pO_2 - t$ curves for different *SCF* samples at 900°C: 2 – powder (56-63 μm, column); 3 – powder (56-63 μm, thin layer); 4 – sintered disk (d=15.5mm; h=1.5mm; m = 1.36g); 5 – coarse particles (1-2 mm, column), $F_{He}$ = 50 ml/min. (1) –the change of $pO_2$ in the reactor without oxygen release, $F_{He}$ = 100 ml/min.

## [5]Influence of the leakage rate and the uncertainty of free reactor volume on the accuracy of the evaluation of the experimental data

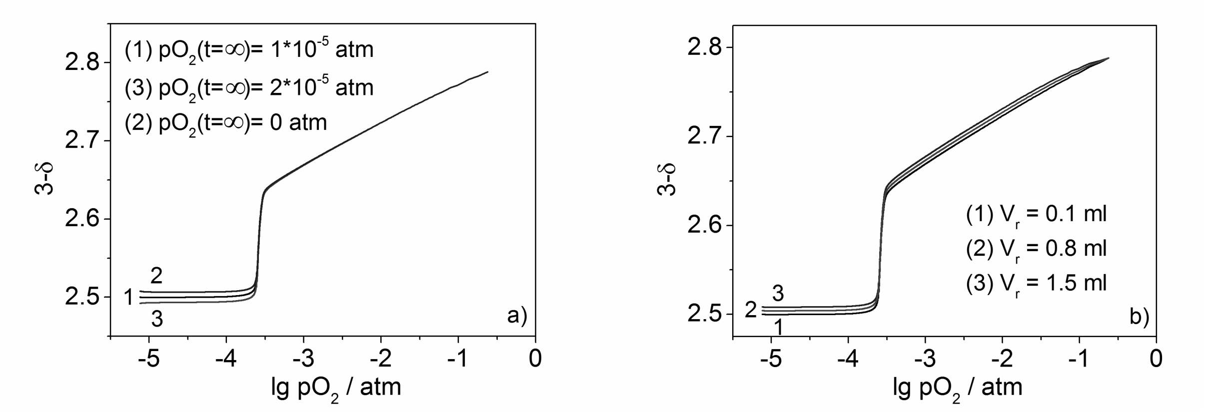

Fig. 6. Influence on the experimental data for *SF* powder sample (T=550 °C, 56-63 μm, m=0.771g) of variation: (a) of leakage rate; (b) - of free reactor volume Vr.

The leakage rate of oxygen affects the background value of $pO_2$ ($pO_2(t=\infty)$) after equilibration oxide with gas phase. According to our estimates, the free volume of the reactor is about 0.1 ml.

## [6] $pO_2$-*t* curves in the case of quasi-equilibrium and non-equilibrium release of oxygen from *SCF* samples, as well as "3-$\delta$-*lg* $pO_2$" diagrams.

### Quasi-equilibrium mode:

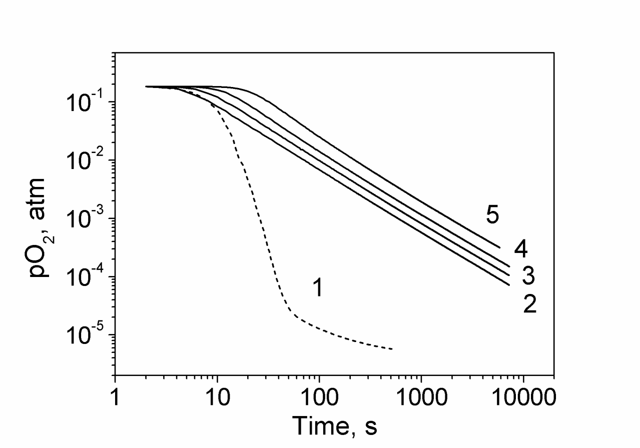

Fig. 7. Dependence of $pO_2$ *vs.* time for *SCF* sintered disk (d=15.5 mm; h=1.5 mm; m = 1.36 g) at 900°C. $F_{He}$ = 100 (2); 70 (3); 50 (4); 30 (5) ml/min. (1) – the change of $pO_2$ in the reactor without oxygen release, $F_{He}$ = 100 ml/min.

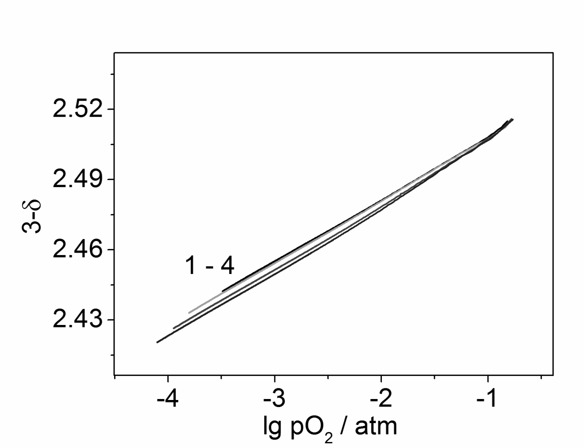

Fig. 8. "3-$\delta$-*lg* $pO_2$" diagrams calculated from data presented on Fig. 6.

### Non-equilibrium mode:

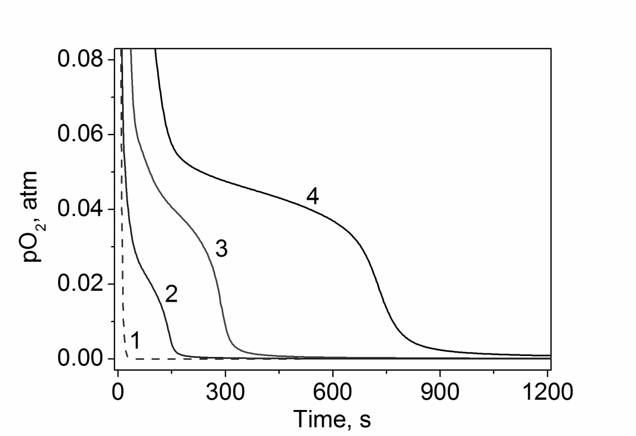

Fig. 9. Dependence of $pO_2$ *vs.* time for *SCF* sintered disk (d=15,5 mm; h=1,5 mm; m = 1,36 g) at 700°C, $F_{He}$ = 100(2), 30(3), 10(4) ml/min. (1) – the change of $pO_2$ in the reactor without oxygen release, $F_{He}$ = 100 ml/min.

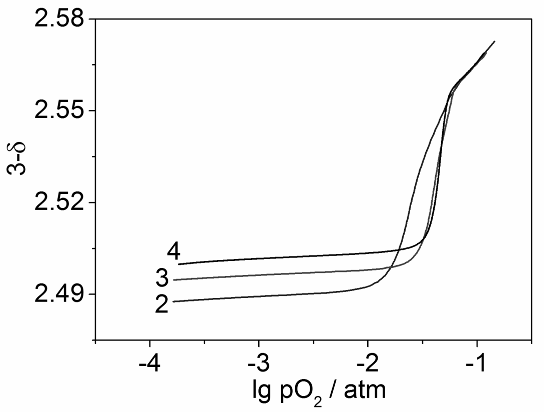

Fig. 10 "3-$\delta$-*lg* $pO_2$" diagrams calculated from data presented on Fig. 8.

## [7]Affine transformation of $pO_2$-*t* curves for SF powdered sample.

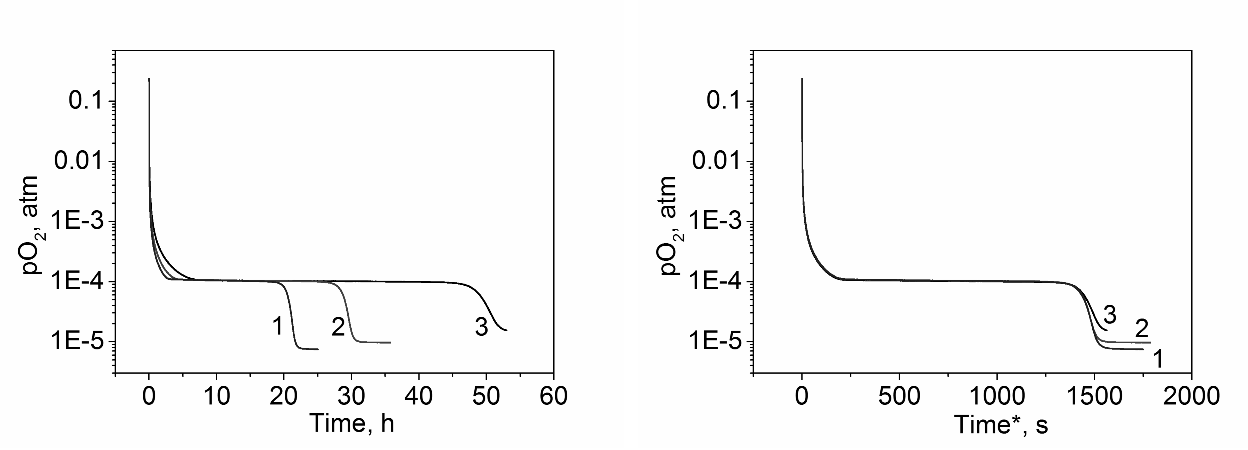

Fig. 11. Dependence of $pO_2$ *vs*. time for *SF* powder sample (56-63 μm, m=0.771g) at 500°C. $F_{He}$ = 70 (1); 50 (2); 30 (3)

Fig. 12. Affine transformation $t^* \rightarrow t \times F_{He} / m$ of $pO_2 - t$ curves presented on Fig. 10

## [8]TG data for *SCF* samples demonstrating the oxygen gain under argon atmosphere

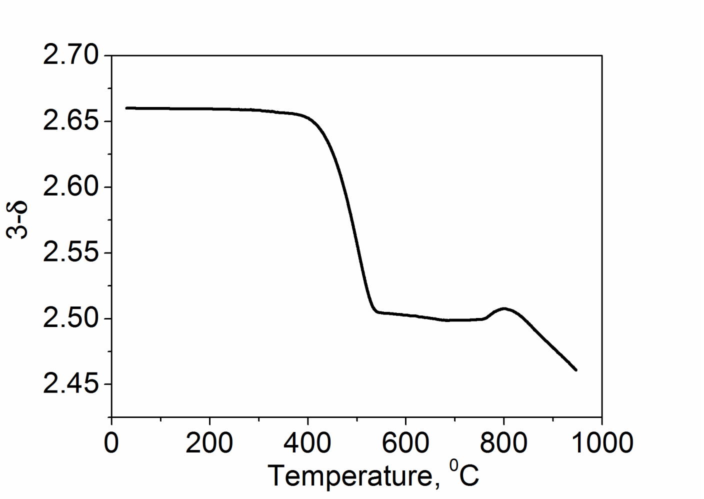

Fig. 13. TG data for SCF in argon flow with $pO_2$~$10^{-2}$ atm (V=10°/min, $F_{Ar}$ = 40 ml/min), at T ~ 800°C there is a noticeable gain of oxygen, which is associated with the morphotropic transition “brownmillerite – perovskite” (compare with TPD-$O_2$ data on Fig.1b obtained at $pO_2$< $10^{-3}$ atm).