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Disorder and transport properties of (Co,Cu,Mg,Ni,Zn)O high entropy oxide

High entropy materials – historical outline

High entropy materials – materials, the structure of which is stabilized by high configurational entropy.

2004 – High entropy alloys

•B. Cantor, I. T. Chang, P. Knight and A. J. Vincent, Microstructural development in equiatomic multicomponent alloys. Materials Science and Engineering: A 2004 Vol. 375-377 pp. 213-218

•J. W. Yeh, S. K. Chen, S. J. Lin, J. Y. Gan, T. S. Chin, T. T. Shun, C. H. Tsau and S. Y. Chang, Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes. Advanced Engineering Materials 2004 Vol. 6 pp. 299-303

2015 – High entropy oxides

C. M. Rost, R. Schaet, T. Borman, A. Moballegh, E. C. Dickey, D. Hou, J. L. Jones, S. Curtarolo and J. P. Maria, Entropy-stabilized oxides. Nature Communications 2015 Vol. 6 pp. 8485

High entropy materials

High entropy alloys – alloys created by mixing at least 5 elements together in approximately identical amounts (5-35% at.). Metal atoms are randomly located in high entropy alloys. The configurational entropy of such a system achieves its maximum value in the case of a solid solution, which facilitates the formation of simple crystalline structures.

High entropy oxides – oxides that constitute a solid solution consisting of at least 5 metal oxides. These materials are interesting due to their transport properties that manifest through e.g. high ionic conductivity.
Potential applications:
Lithium batteries, solid oxide fuel cells (SOFC)

High entropy oxides

High entropy oxides may have practical use due to the point defect structure and mobility of these oxides.

Becoming familiar with the transport properties of these materials will enable the possibility of maximizing their hidden potential and making them a valuable group of new materials that constitute a basis for future energy-creating technology.

Research goal

The aim of this work was to obtain information concerning the type and magnitude of the predominant disorder, as well as chemical diffusion, present inside a (Co,Cu,Mg,Ni,Zn)O high entropy oxide.

Experimental procedure

Initial materials for investigations (powders):
Co_3O_4, CuO, MgO, NiO, ZnO,

purity > 99,9 % at.; granulation 0,044 ÷ 0,250 µm

Milling:
90 min, 600 rot/s, planetary mill (Fritsch Pulverisette 7)

Pressing:
dics: Φ = 10 mm, h = 2 mm, pressure: 2 t

Sintering:
20 h, 1273 K, cooling on a cold aluminium plate

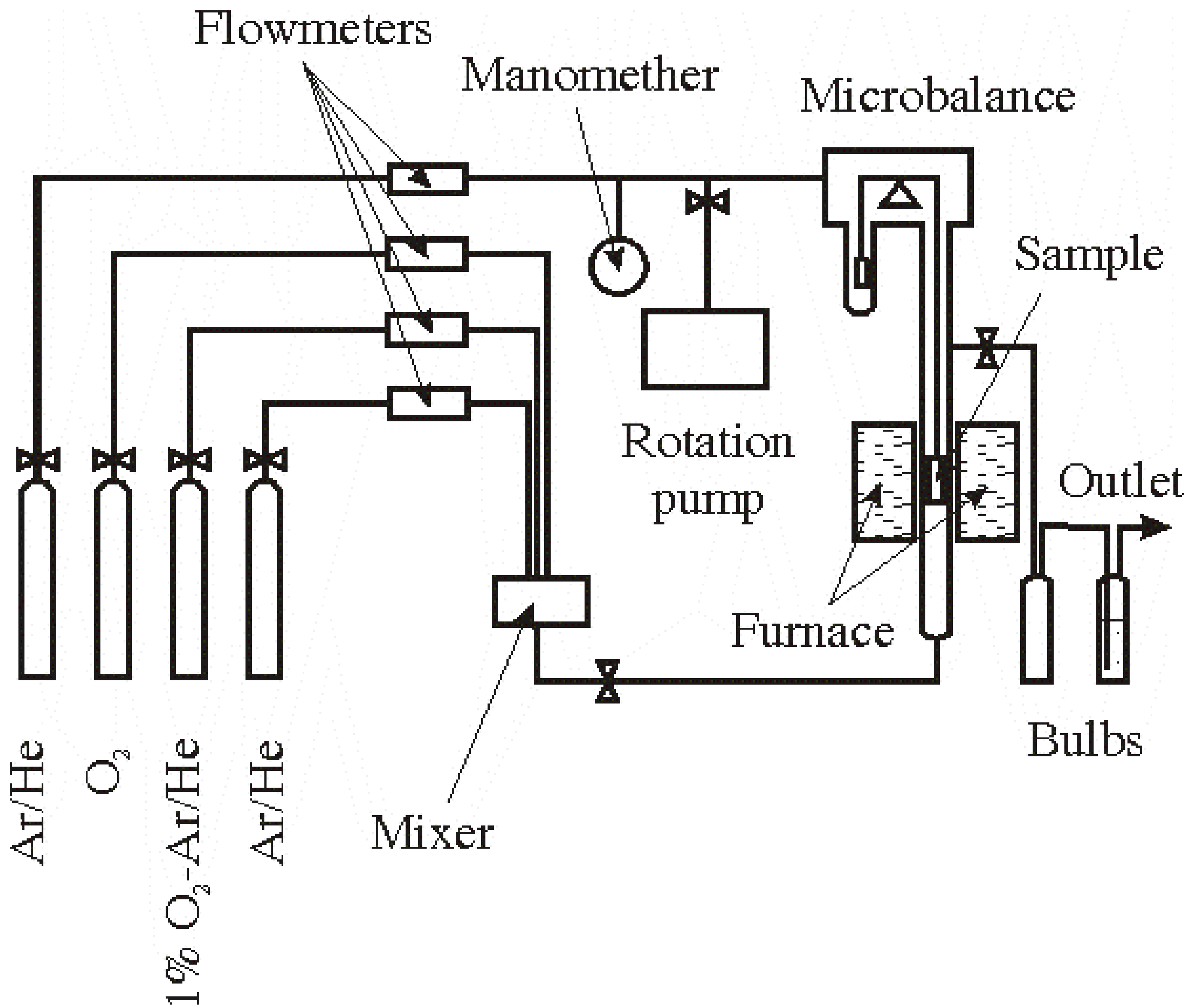
Microstructural studies:
XRD, SEM+EDS

Marker investigations:
Au, 1173 K,

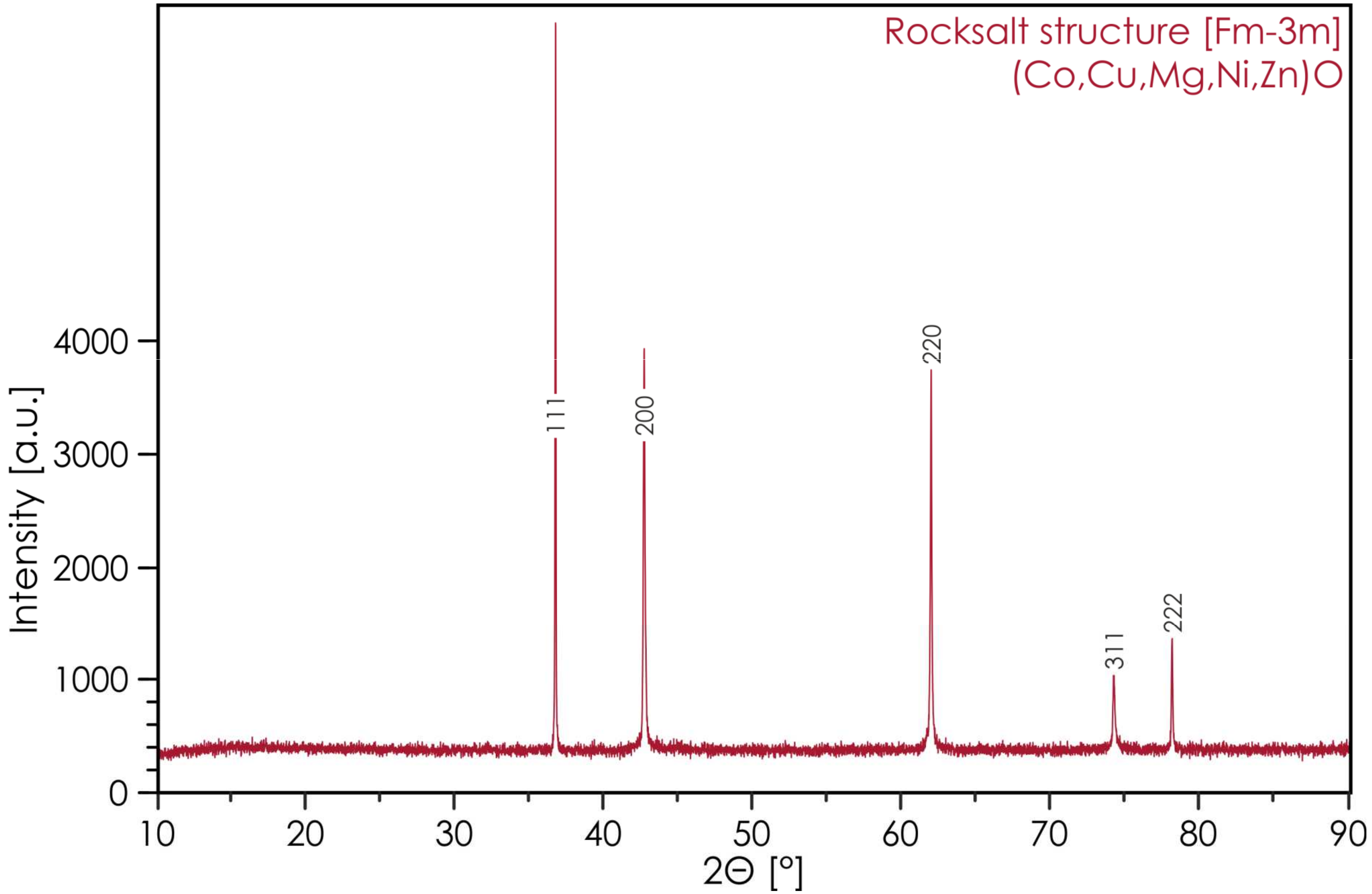
Deviation from stoichiometry studies:
1173 K, 10-10^5 Pa (thermogravimetric method)

Chemical diffusion investigations:
1173 K, 10-10^5 Pa (re-equilibration method)

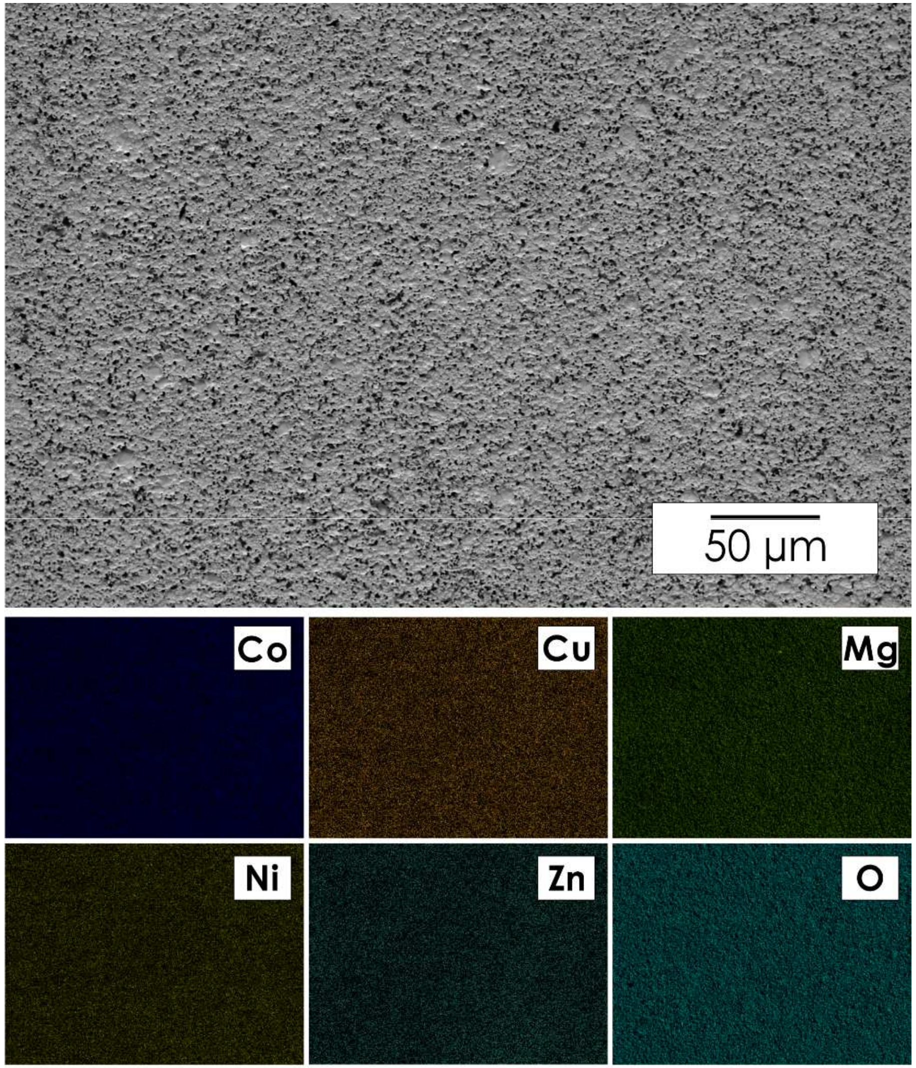
Scheme of the microthermogravimetric apparatus for defect concentration and mobility studies



XRD analysis performed on the surface of a (Co,Cu,Mg,Ni,Zn)O oxide sample



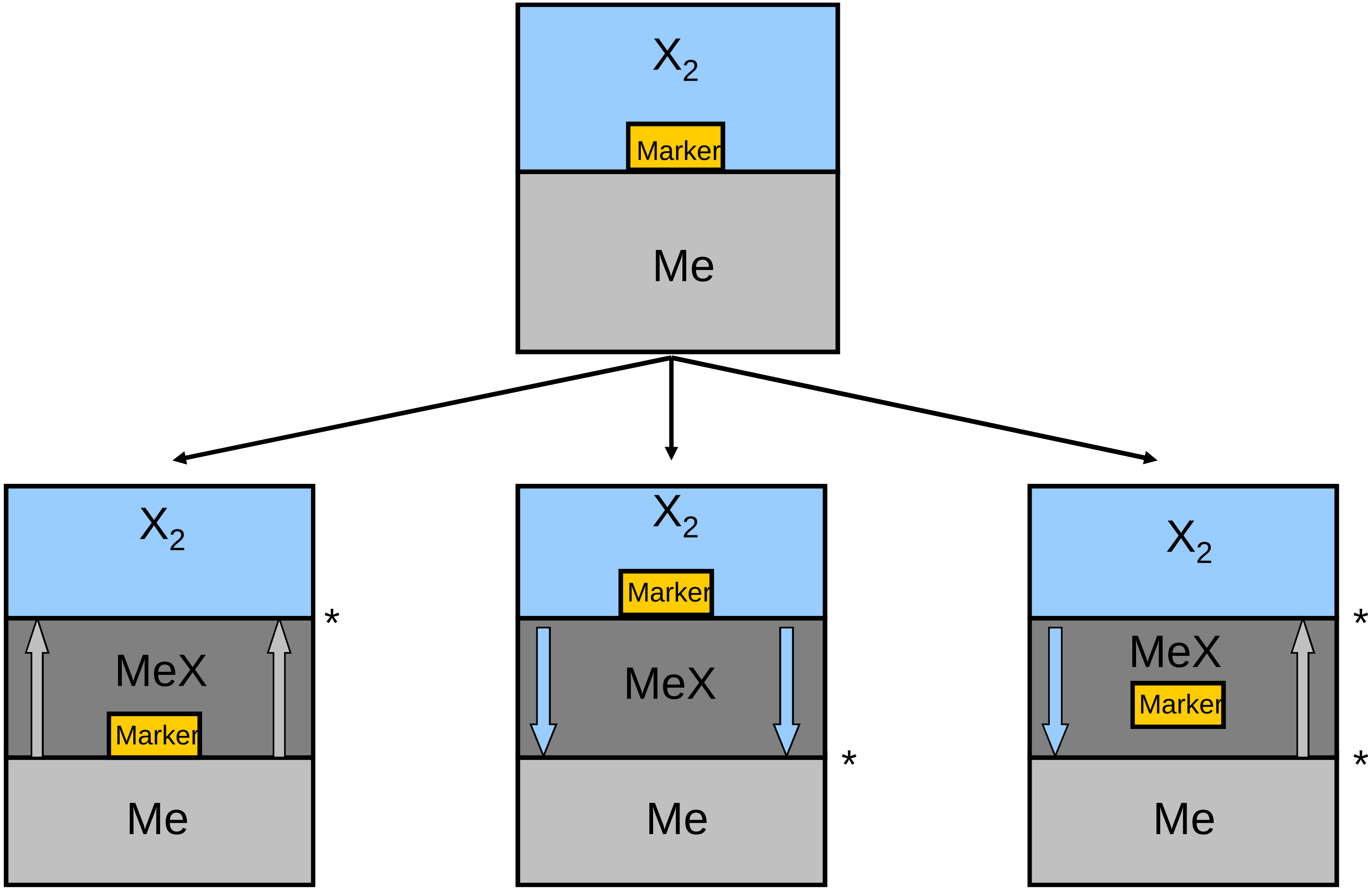
EDS analysis carried out on the surface of a (Co,Cu,Mg,Ni,Zn)O oxide sample



Analiza powierzchniowa EDS [% at. ±0.1%]					
Co	Cu	Mg	Ni	Zn	O
11,2	10,2	10,7	11,3	10,3	46,3

Marker method in metal-oxide systems

Determining the MeX sublattice with predominant disorder



cation sublattice

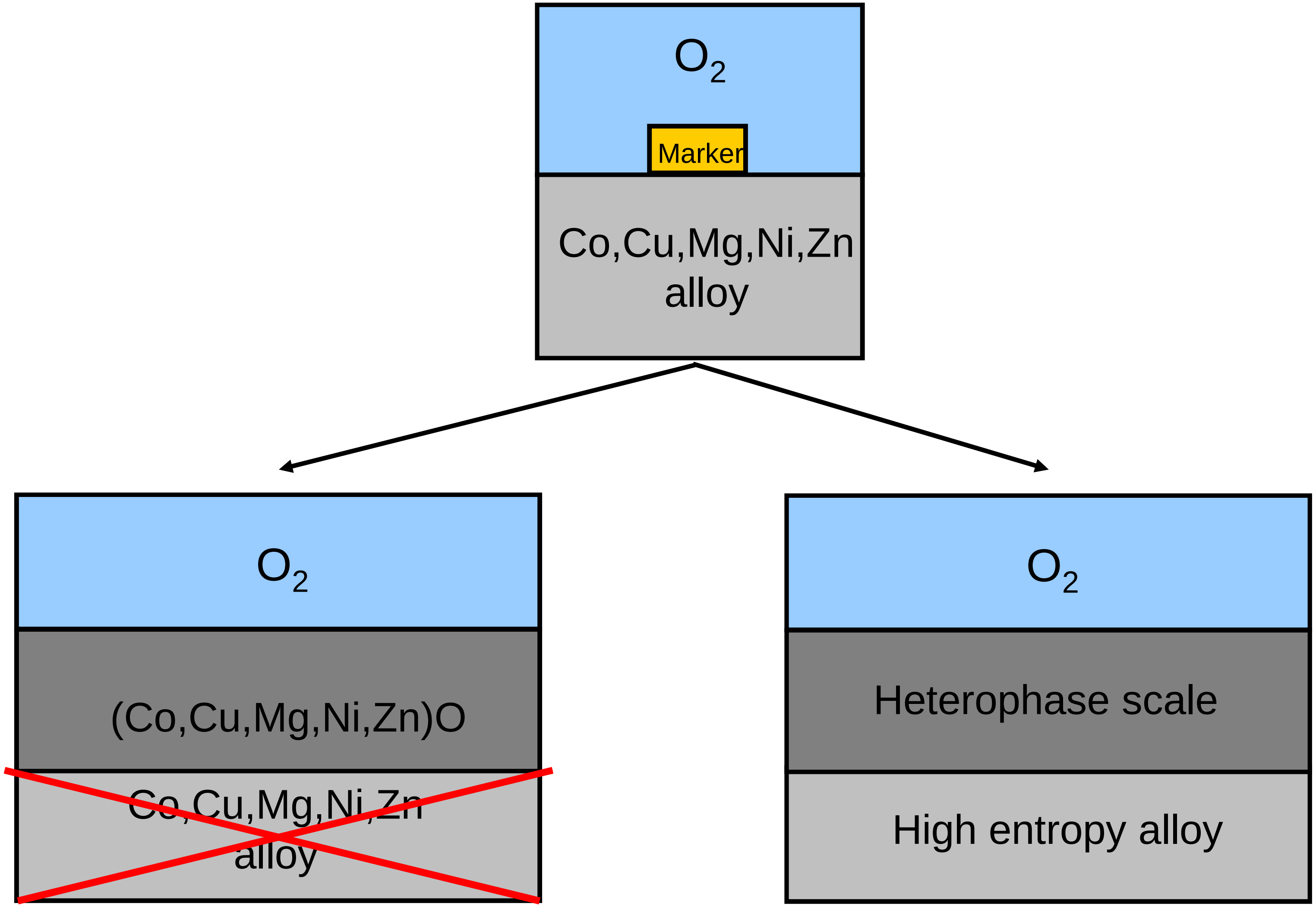
anion sublattice

cation sublattice
anion sublattice

* Location of the reaction: $\frac{1}{2}X_2 + Me \rightarrow MeX$

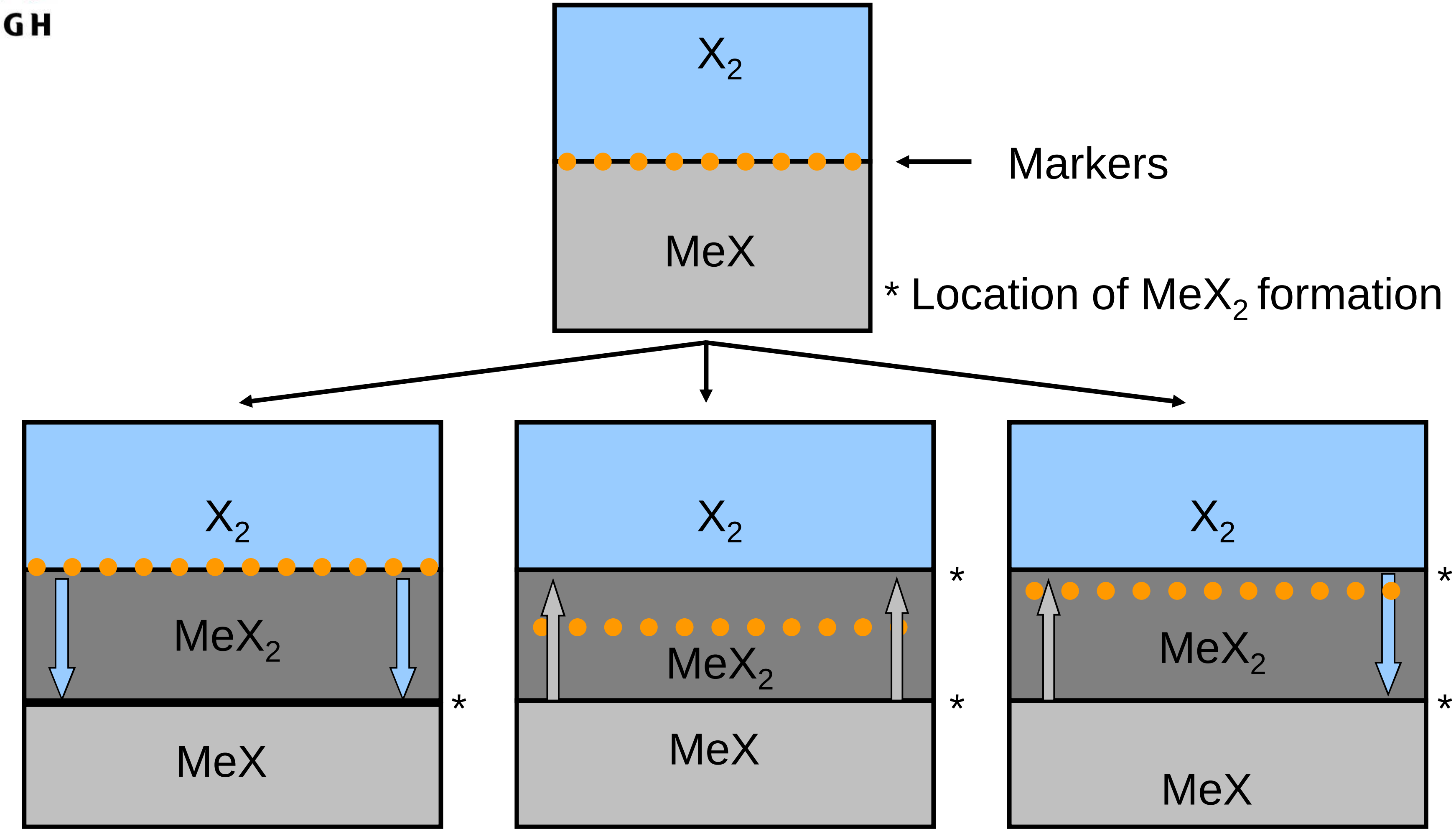
Marker method

Oxidation of Co,Cu,Mg,Ni,Zn high entropy alloy



Marker method in oxide-oxidant systems

Determining the MeX_2 sublattice with predominant disorder



* Location of MeX_2 formation

anion sublattice

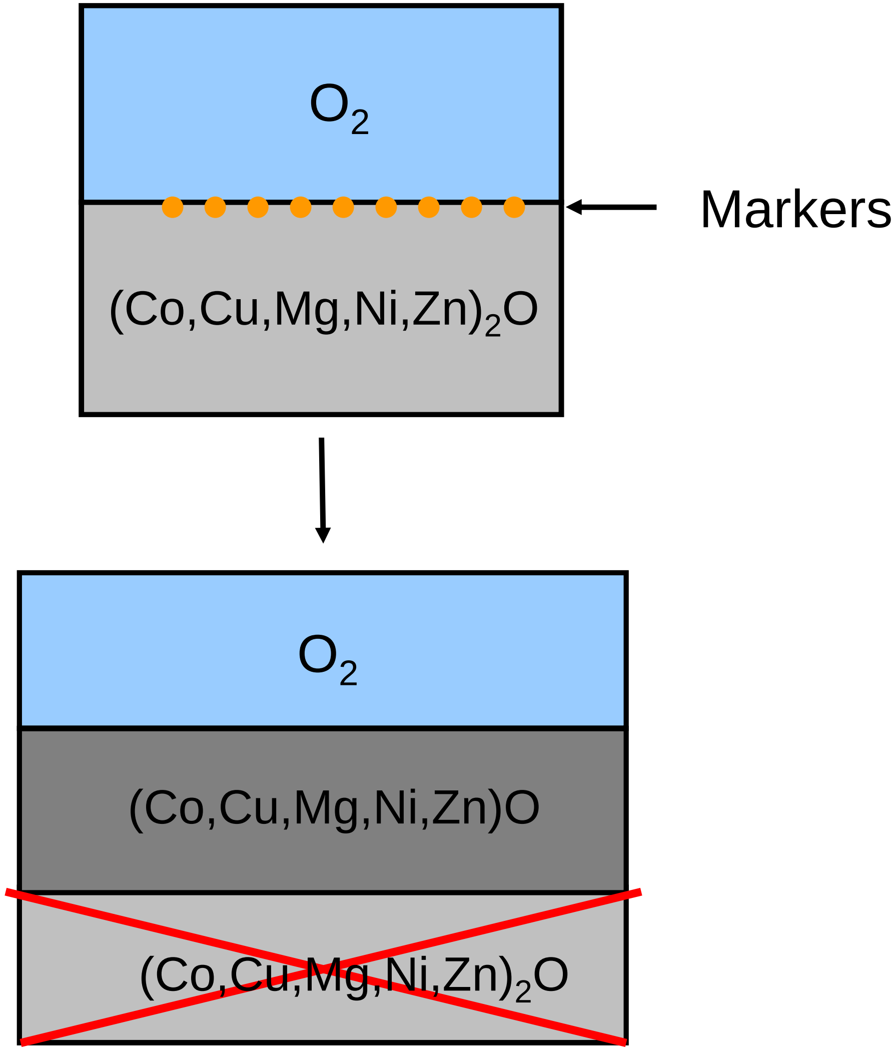
cation sublattice

cation sublattice
anion sublattice

Z. Grzesik, A. Poczekajlo, G. Smola, S. Mrowec, „Marker method in studying the defect structure in products of the oxidation of highly disordered substrates”, High Temperature Materials and Processes, 35, 21-28 (2016)

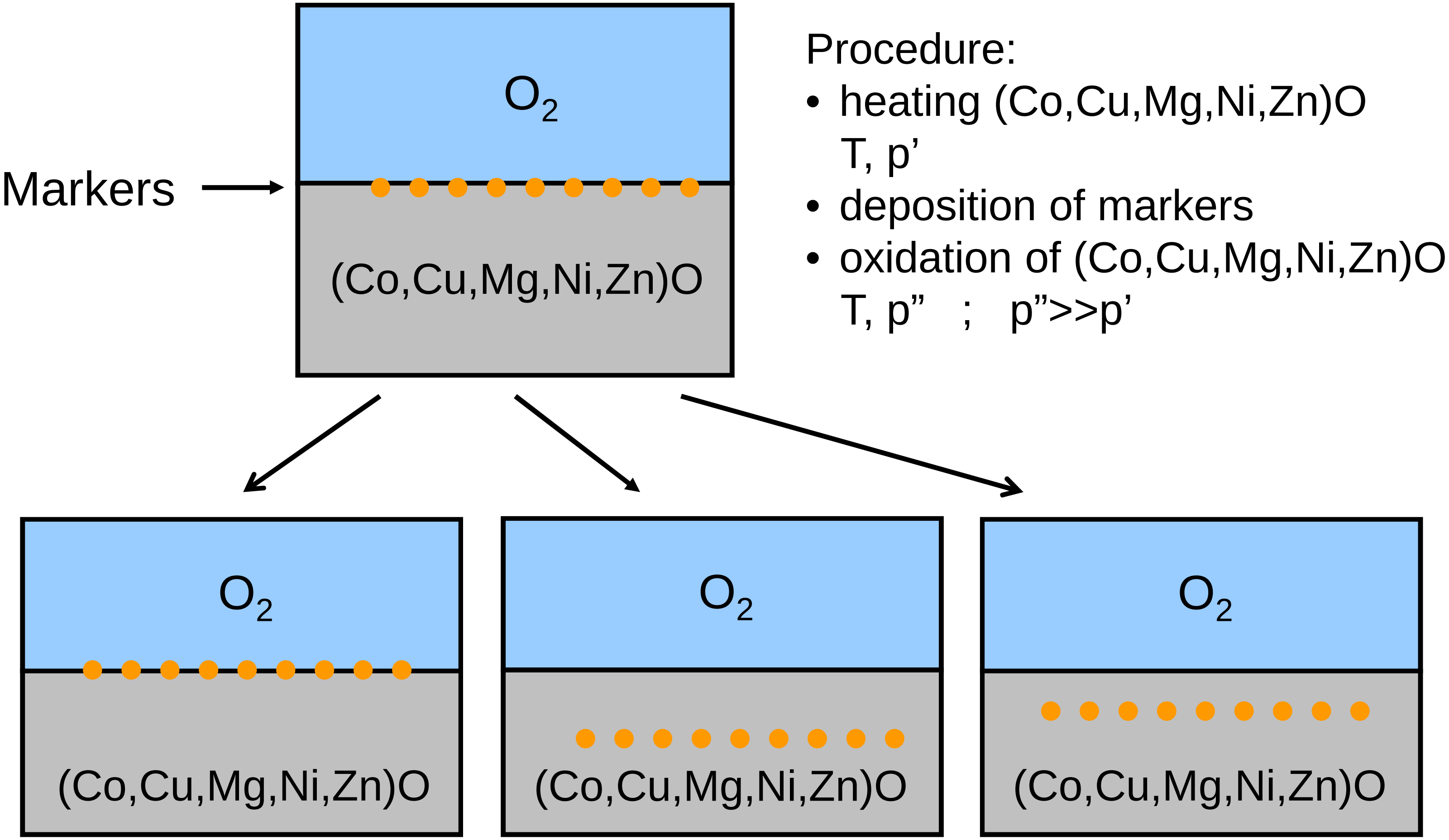
Marker method

Oxidation of $(Co,Cu,Mg,Ni,Zn)_2O$ oxide



Modified marker method

Oxidation of (Co,Cu,Mg,Ni,Zn)O oxide



Procedure:

- heating (Co,Cu,Mg,Ni,Zn)O
  T, p’
- deposition of markers
- oxidation of (Co,Cu,Mg,Ni,Zn)O
  T, p”   ;   p”>>p’

disorder:
anion sublattice

$$\frac{1}{2}X_{2(g)} \Leftrightarrow X_i^{''} + 2h^{\bullet}$$

$$MeX \Leftrightarrow V_X^{\bullet\bullet} + 2e^{'} + Me_{Me}^{x} + \frac{1}{2}X_{2(g)}$$

disorder:
cation sublattice

$$M_M^x + X_X^x \Leftrightarrow M_i^{\bullet\bullet} + 2e^{'} + \frac{1}{2}X_{2(g)}$$

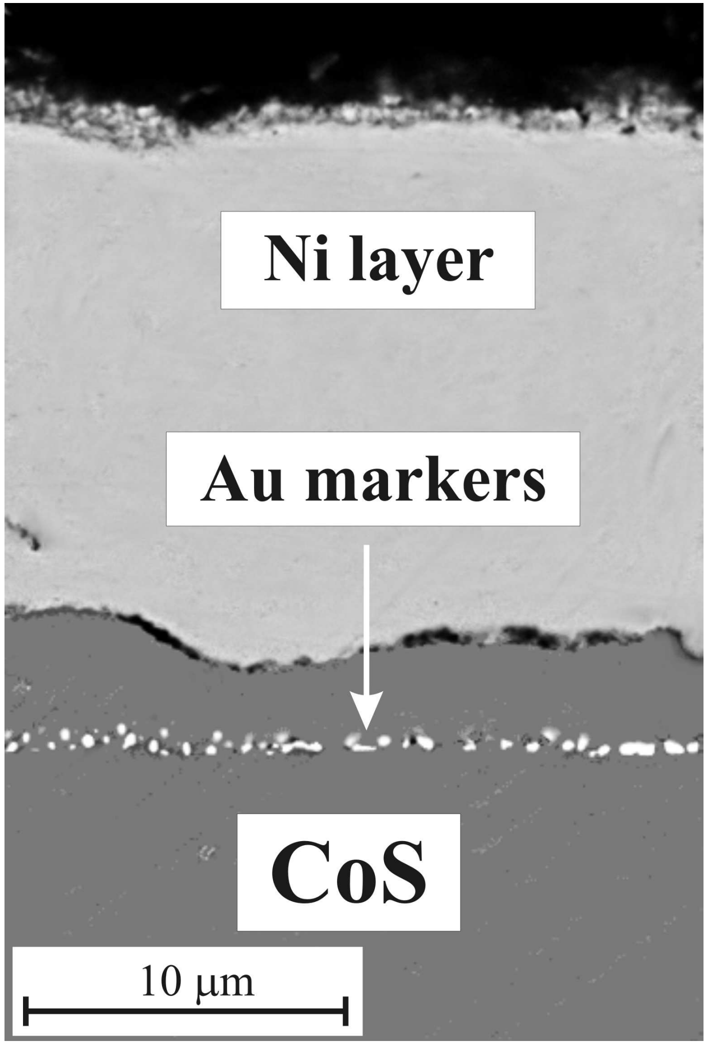
$$\frac{1}{2}X_{2(g)} \Leftrightarrow V_M^{''} + 2h^{\bullet} + X_X^x$$

disorder:
cation sublattice

anion sublattice

4 defect reactions

Modified marker method
– location of markers in CoS

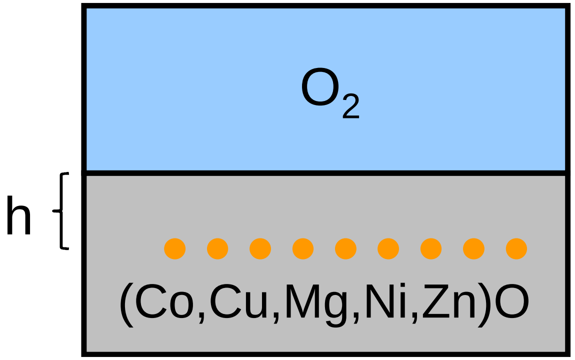


Z. Grzesik, A. Poczekajlo, G. Smola, S. Mrowec, „Marker method in studying the defect structure in products of the oxidation of highly disordered substrates”, High Temperature Materials and Processes, 35, 21-28 (2016)

Modified marker method

Oxidation of (Co,Cu,Mg,Ni,Zn)O oxide

Assumption:
Predominant disorder is present in the cation sublattice



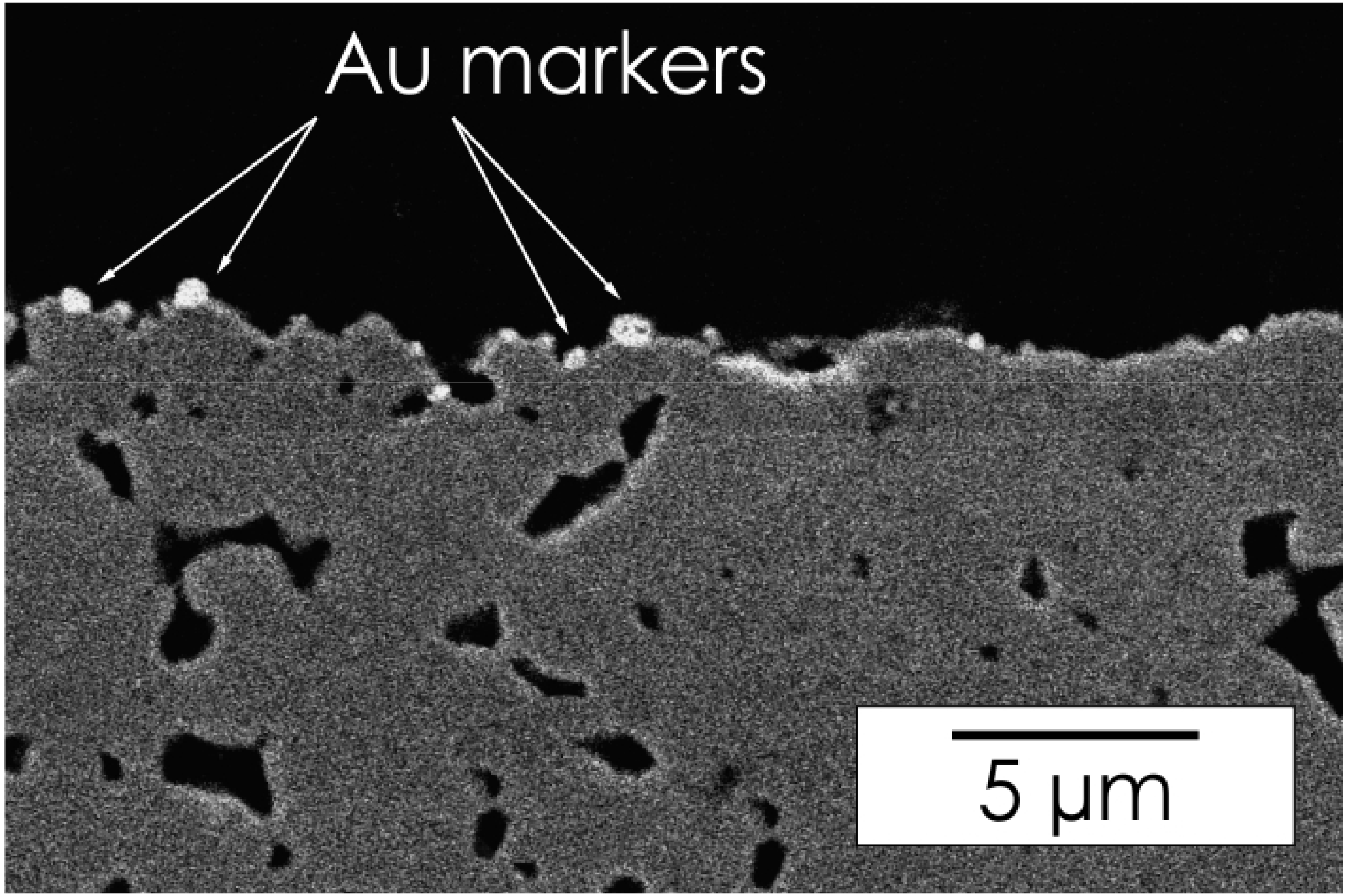
Data:
Sample parameters after heating
(1173 K, p_{O2}= 10 Pa):
mass = 0,4336 mg
diameter = 10 mm
height = 1,57 mm

Sample mass change after oxidation
(1173 K, p_{O2}= 10^5 Pa): 7 mg

h = 12 μm

Conclusion:
In the case of predominant disorder in the cation sublattice, markers should be located 12 micrometers below the oxide surface.

(Co,Cu,Mg,Ni,Zn)O sample cross-section after completing modified marker studies



Necessary conditions for obtaining positive results by means of the modified marker method

- Before marker deposition, the oxide sample must be heated under lower oxygen pressure compared to the pressure used during oxidation of the sample covered with markers.
- The change in deviation from stoichiometry of a studied oxide during a marker experiment must be large (order of a few percent).
- Sample thickness should exceed 1 mm.
- The duration of defect concentration re-equilibration during oxygen pressure changes should be several times longer than ~1 min (this means that the chemical diffusion coefficient is low and/or the sample thickness is large).

Conclusion:

A full interpretation of a modified marker experiment is possible after completing both marker studies, as well as point defect concentration and mobility investigations inside a given oxide.

Determining deviation from stoichiometry in MeX_{1-y}-type oxides using the gravimetric method when the metal content in the sample is known

$$y = 1 - \frac{m_O M_{Me}}{m_{Me} M_O}$$

where:

m_{Me} – mass of the metal in an oxide sample

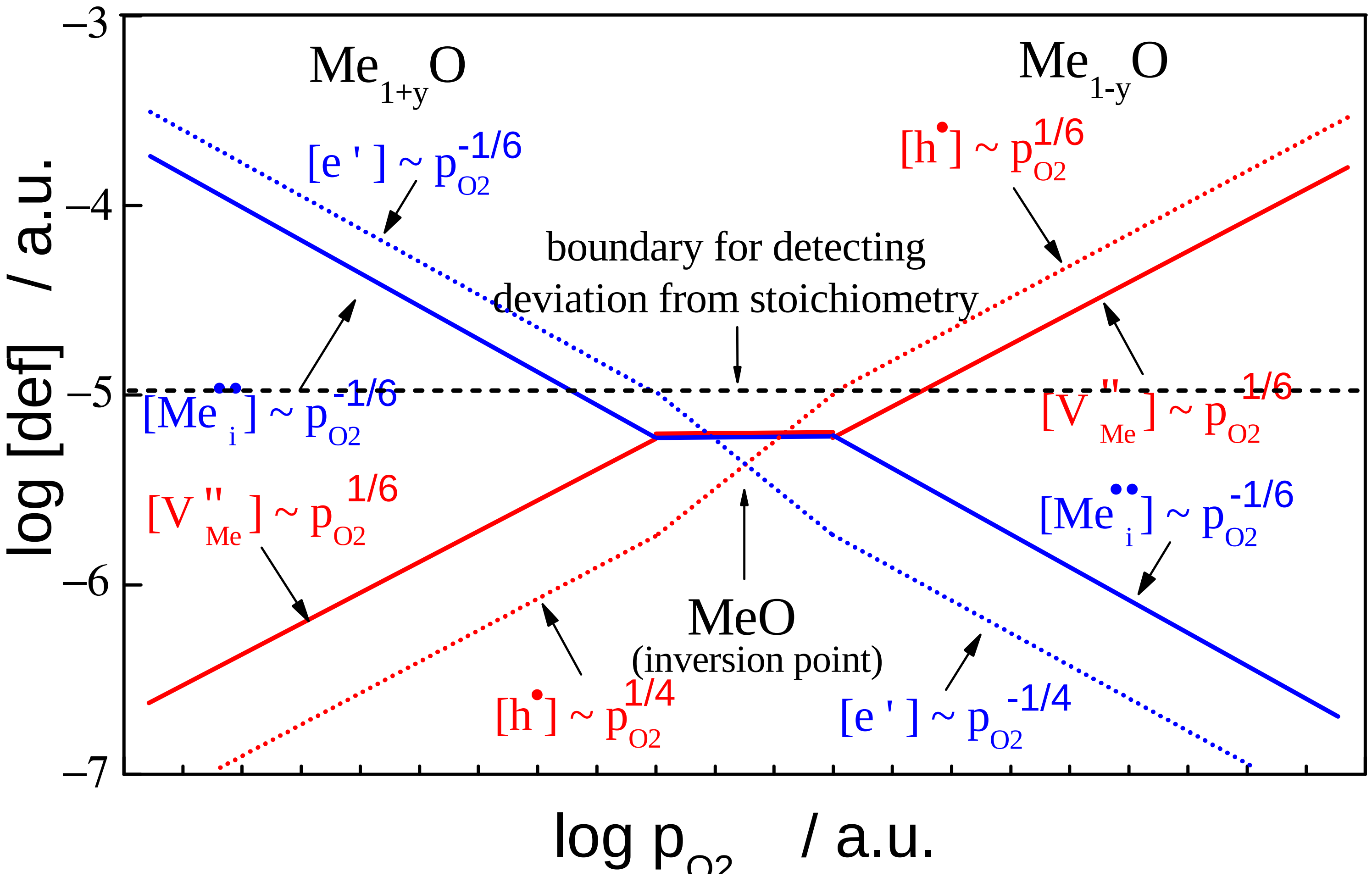
m_O – oxygen mass in an oxide sample

M_{Me} i M_O – atomic masses of metal and oxygen.

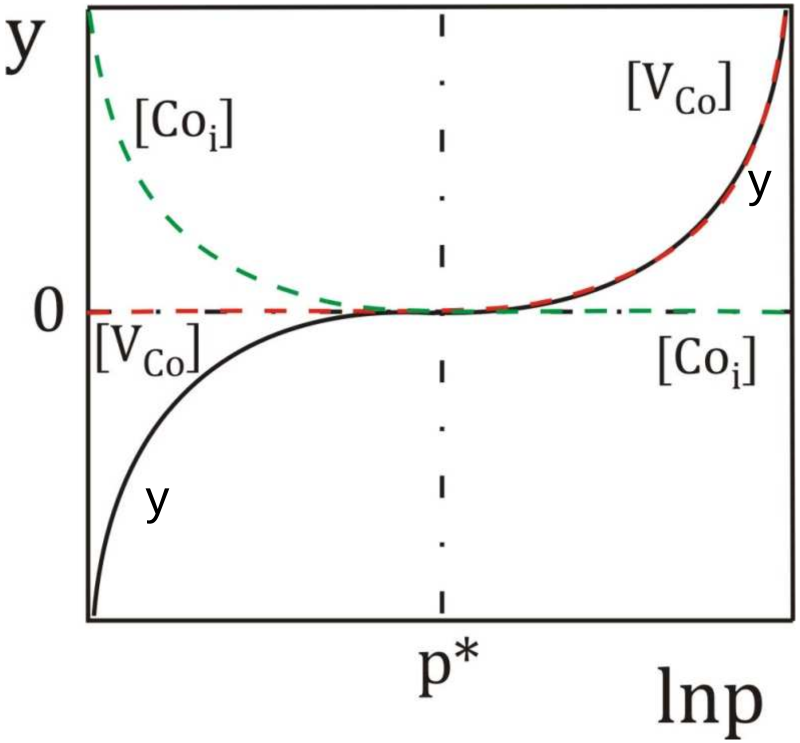
Methods for determining deviation from stoichiometry in oxides with unknown metal content

- oxide reduction to pure metal (e.g. in hydrogen atmosphere, electrochemical reduction, etc.)
- subjecting the oxide to a reaction with a different oxidant (e.g. with sulphur)
- using a reference sample with a known metal mass
- assuming certain thermodynamic parameters (T, p), at which oxide sample mass changes are not observed along with parameter modifications, that allow for the oxide to exhibit a stoichiometric composition, as long as the sample mass changes in a different range of parameter modifications.

Scheme of the correlation between defect concentration and oxidant pressure in an oxide with a complex defect structure



Schematic illustration of pressure dependence of deviation from stoichiometry in Co $_{3\pm y}O_4$



$$Co_3\,O_4 \Leftrightarrow 3Co_i^{8/3\bullet} + 8e' + 2O_2$$

$$\left[Co_i^{8/3\bullet}\right] = a \cdot p_{O_2}^{-2/3}$$

$$2O_2 \Leftrightarrow 3V_{Co}^{8/3'} + 8h^{\bullet} + 4O_O^X$$

$$\left[V_{Co}^{8/3'}\right] = b \cdot p_{O_2}^{2/3}$$

$$y = \left[V_{Co}^{8/3'}\right] - \left[Co_i^{8/3\bullet}\right] = b \cdot p^{\frac{2}{3}} - a \cdot p^{-\frac{2}{3}}$$

$$p = p^* = \left(\frac{a}{b}\right)^{\frac{3}{4}}$$

p* - oxygen pressure, at which $Co_{3\pm y}O_4$ oxide is strictly stoichiometric (y = 0)

Z. Grzesik, A. Kaczmarska, „Defect structure of Co_3O_4 cobalt oxide”, Ann. Chim. Sci. Mat. 40 (1-2), 103-109 (2016).

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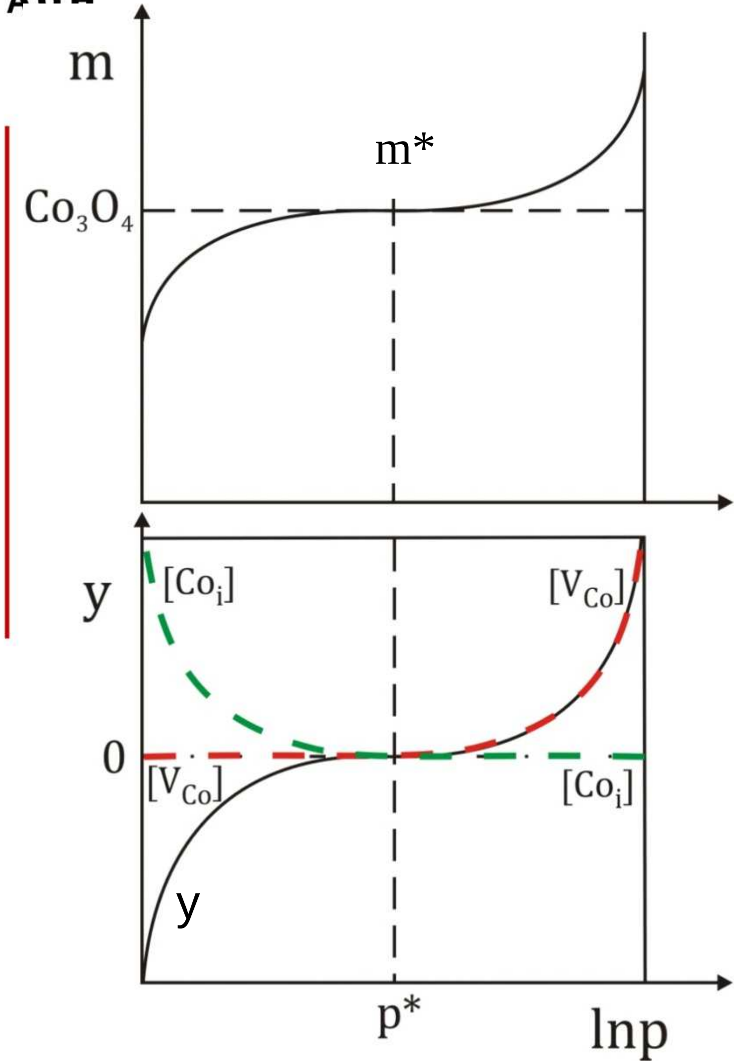
$Co_{3\pm y}O_4$ sample mass changes and deviation from stoichiometry, y, as a function of oxygen pressure



Assumption:

m = f(ln p) and y = f(ln p) curves exhibit an inflection point for p*

$$p = p^* = \left(\frac{a}{b}\right)^{\frac{3}{4}}$$

Proof:

The second derivative of m = f(ln p) and y = f(ln p) is equal to zero for p* and in the vicinity of p* both functions change their sign

$$\frac{d^2y}{d(\ln p)^2} = 0 \quad \Rightarrow \quad b \cdot p^{\frac{2}{3}} - a \cdot p^{-\frac{2}{3}} = 0 \quad \Rightarrow \quad p = p^* = \left(\frac{a}{b}\right)^{\frac{3}{4}}$$

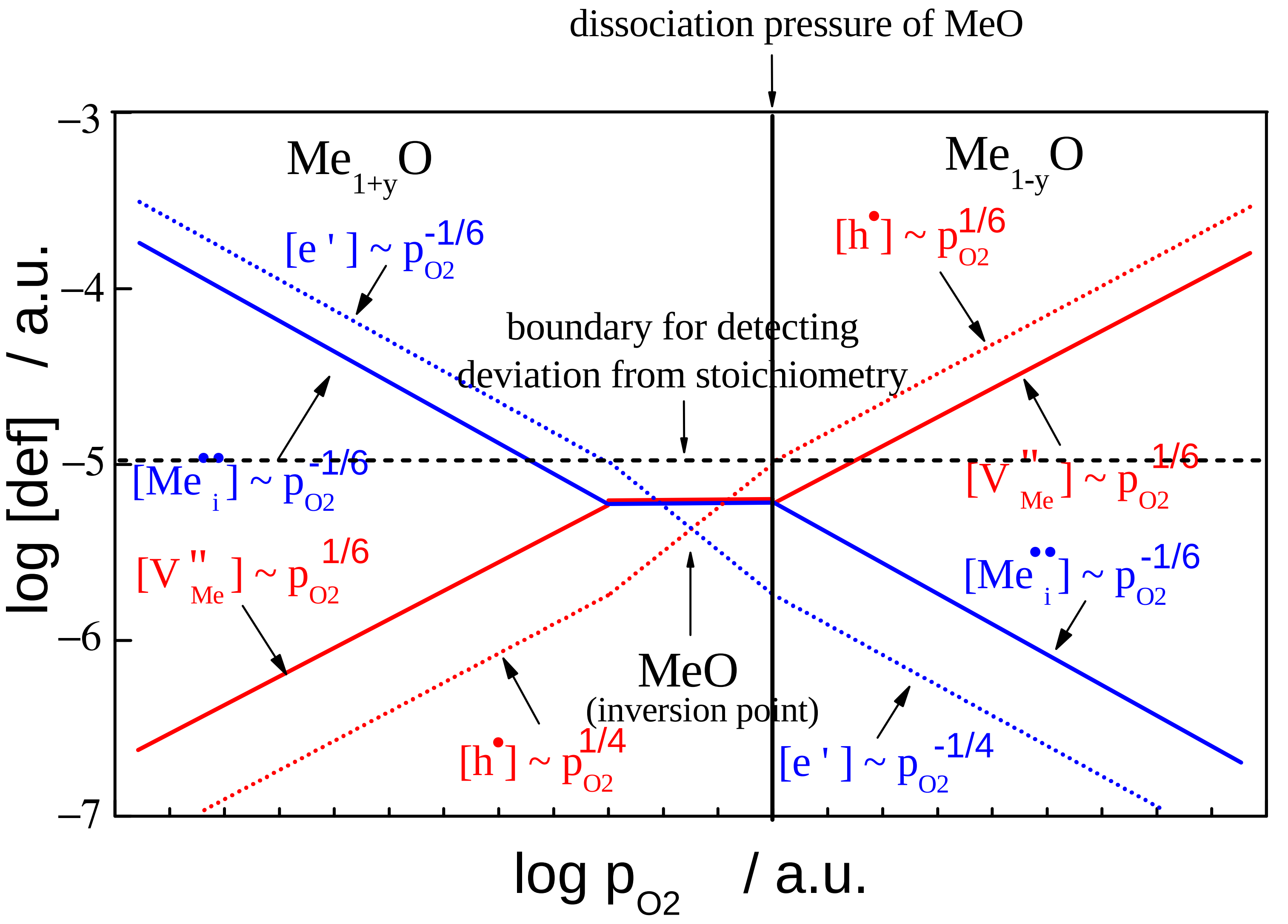
$$m = m^* + \frac{4}{3} M_O \cdot b \cdot p^{\frac{2}{3}} - \frac{4}{3} M_O \cdot a \cdot p^{-\frac{2}{3}}$$

where m* denotes the mass of a stoichiometric Co_3O_4, and M_0 is the atomic mass of oxygen

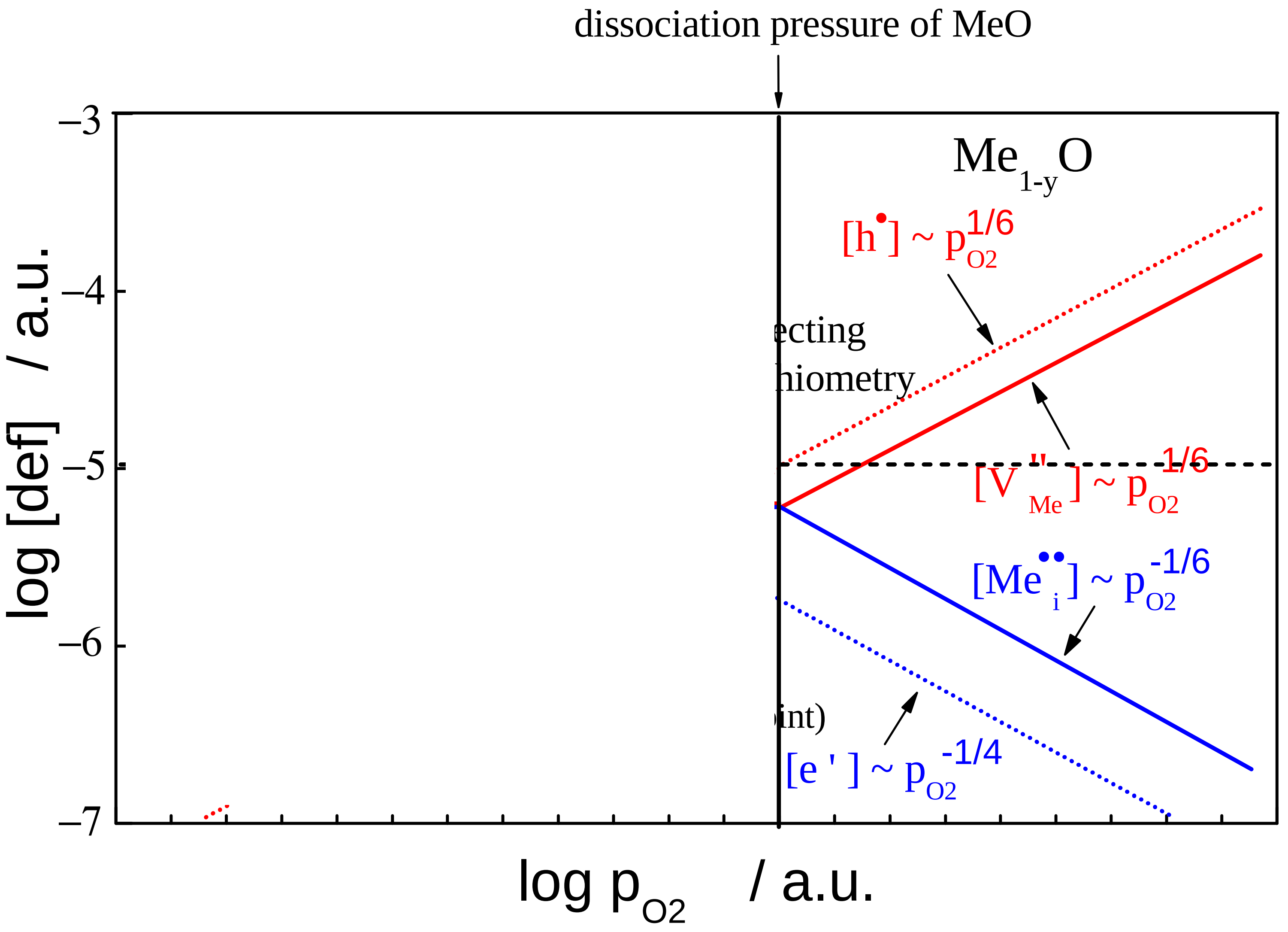
$$\frac{d^2\Delta m}{d(\ln p)^2} = \frac{4}{3} M_O \cdot \left(\frac{4}{9} b \cdot p^{\frac{2}{3}} - \frac{4}{9} a \cdot p^{-\frac{2}{3}} \right) = 0 \quad \Rightarrow \quad p = p^* = \left(\frac{a}{b}\right)^{\frac{3}{4}}$$

Z. Grzesik, A. Kaczmarska, „Defect structure of Co_3O_4 cobalt oxide”, Ann. Chim. Sci. Mat. 40 (1-2), 103-109 (2016).

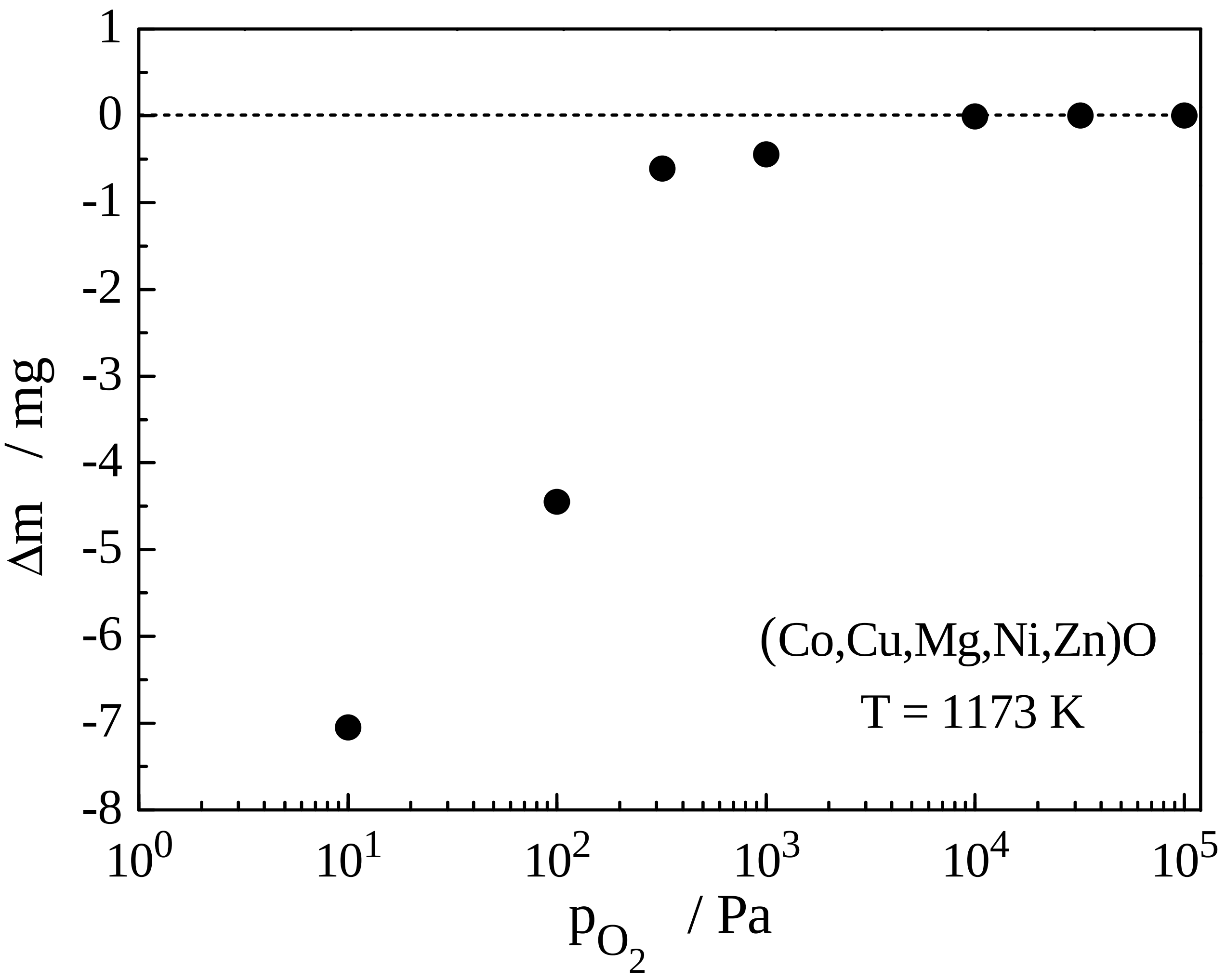
Oxidant pressure dependence of defect concentration in an oxide with a simple defect structure



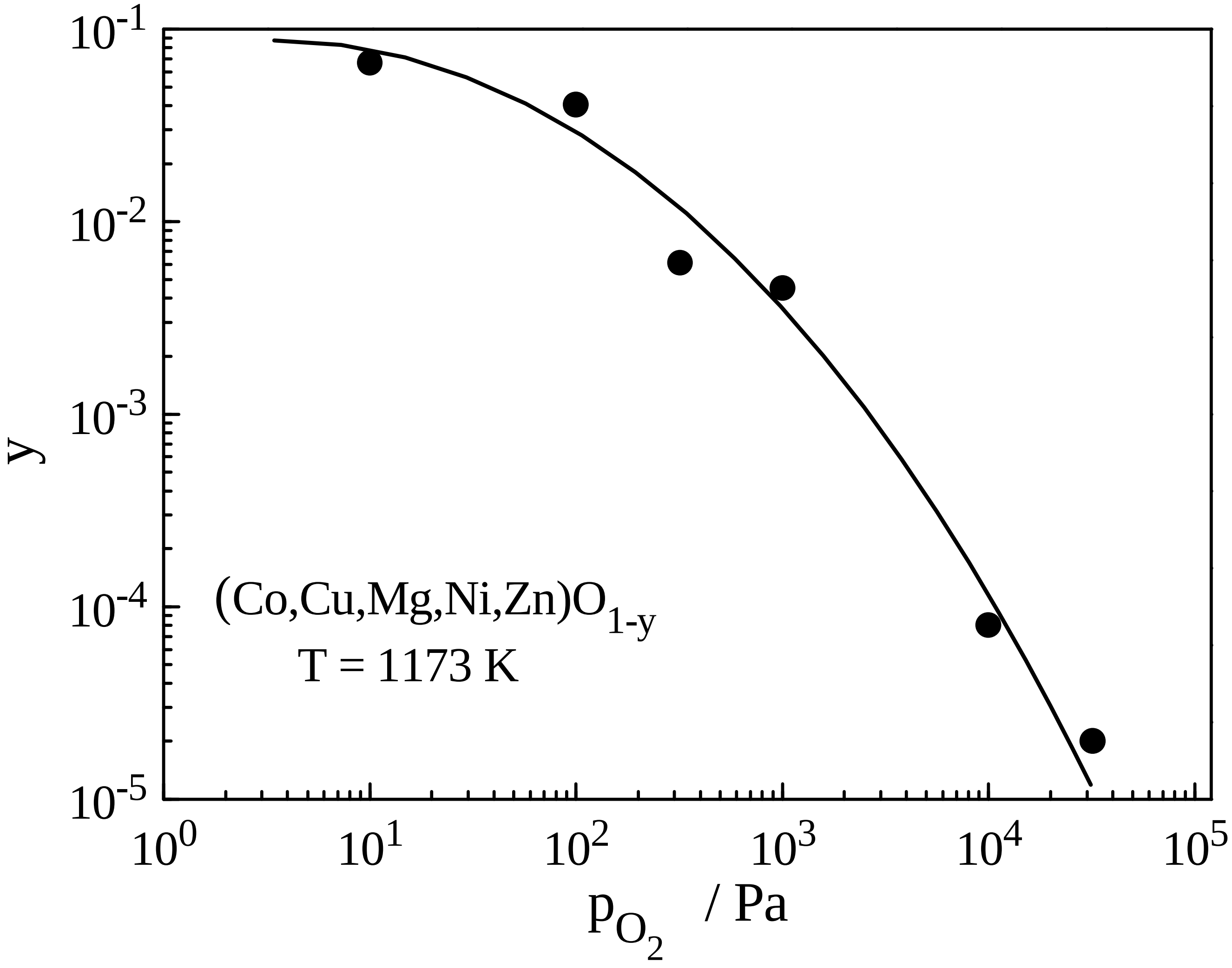
Oxidant pressure dependence of defect concentration in an oxide with a simple defect structure



Correlation between (Co,Cu,Mg,Ni,Zn) O sample mass change and oxygen pressure



Pressure dependence of deviation from stoichiometry, y, in (Co,Cu,Mg,Ni,Zn) O_{1-y}



Maximum values of deviation from stoichiometry in selected metal oxides

$T = 1173$ K, $p_{O2} = 10^{5}$ Pa

$(Co,Cu,Mg,Ni,Zn)\,O_{1-y}$: $y = 0,07$

$Co_{3\pm y}O_4$: $y < 10^{-5}$
$Cu_{1\pm y}O$: $y < 10^{-5}$
$Mg_{1\pm y}O$: $y < 10^{-5}$
$Ni_{1-y}O$: $y = 10^{-4}$
$Zn_{1+y}O$: $y < 10^{-5}$

Determining chemical diffusion coefficients of defects by means of re-equilibration technique

$\tilde{D}t/a^2 < 0{,}25:$

$$\left(\frac{\Delta m_t}{\Delta m_k}\right)^2 = \frac{4\tilde{D}t}{\pi a^2}$$

$\tilde{D}t/a^2 > 0{,}15:$

$$1 - \frac{\Delta m_t}{\Delta m_k} = \frac{8}{\pi^2}\exp\left(-\frac{\tilde{D}\pi^2 t}{4a^2}\right)$$

where:

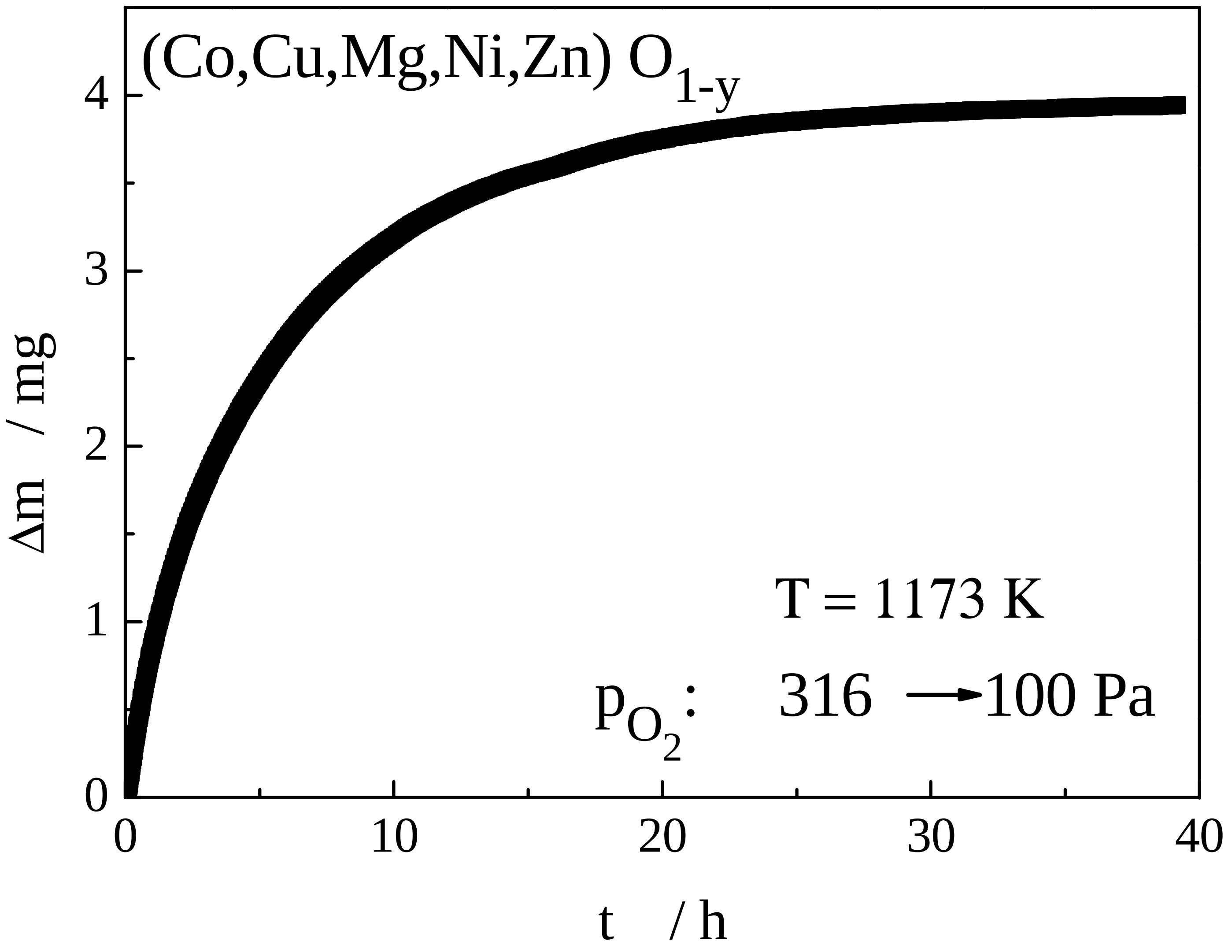
Δm_t – sample mass change after duration t

Δm_k – total sample mass change

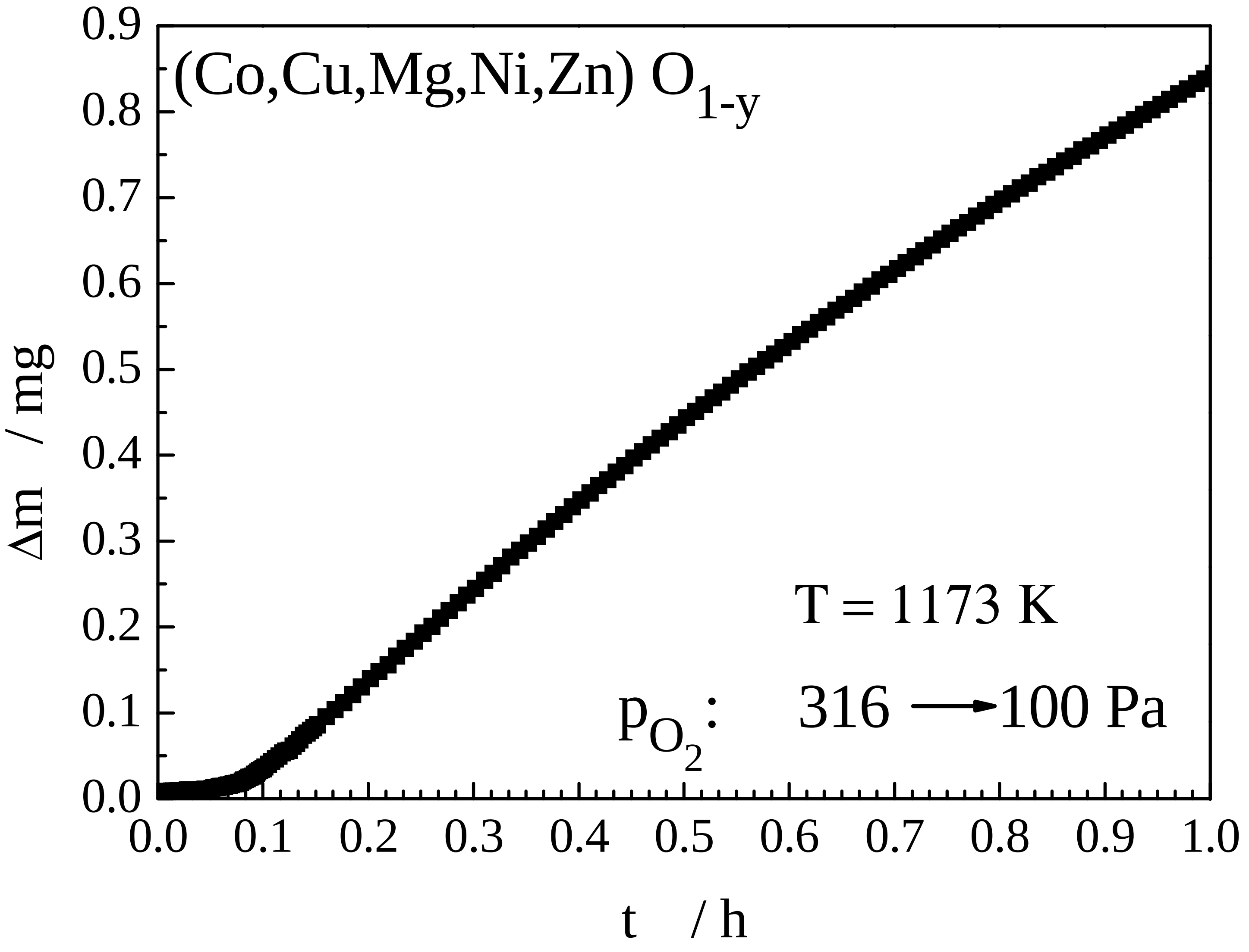
a – half of the sample thickness

$\tilde{D}$ – chemical diffusion coeffcient

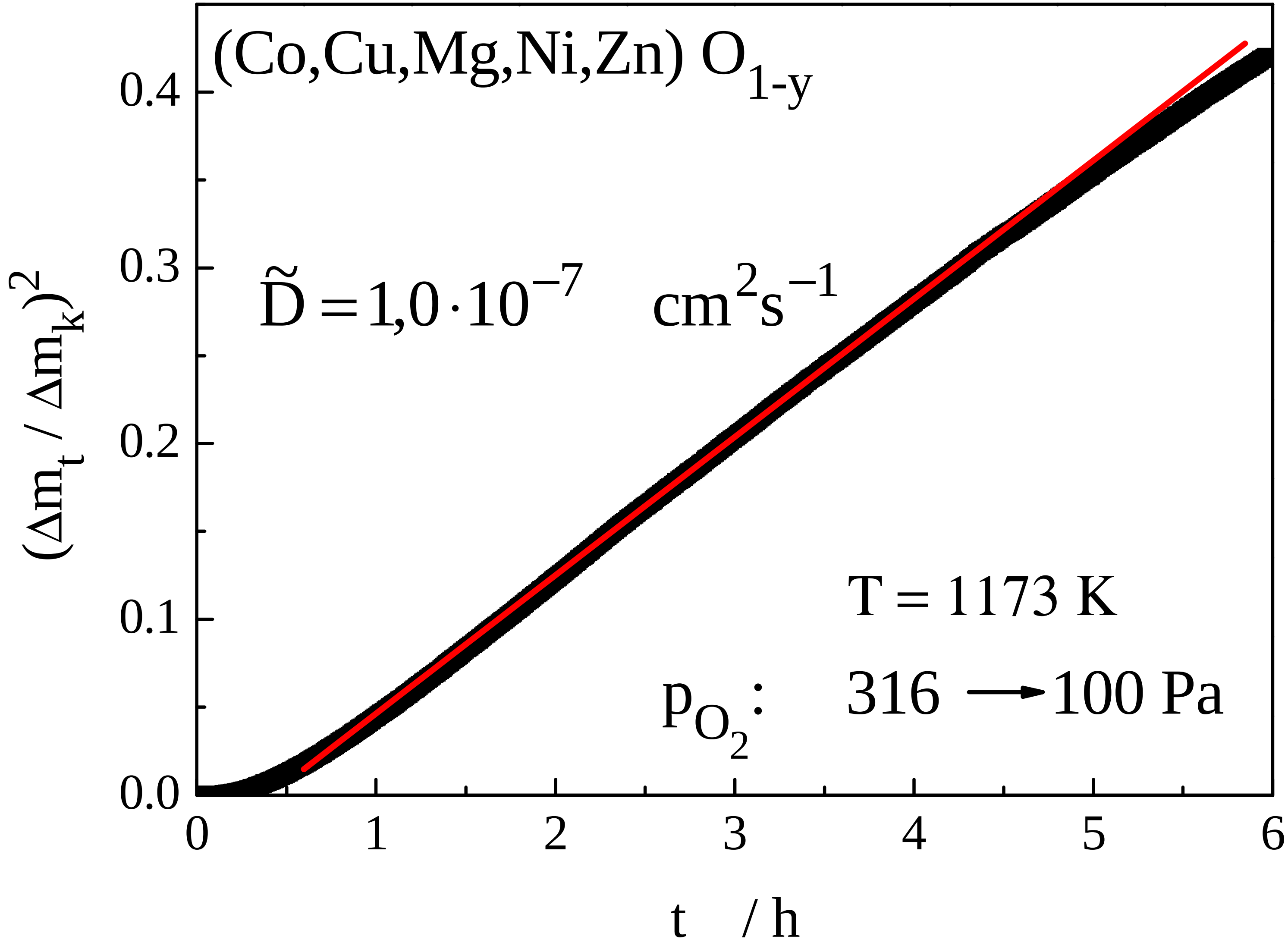
Reduction kinetics of (Co,Cu,Mg,Ni,Zn) O_{1-y}



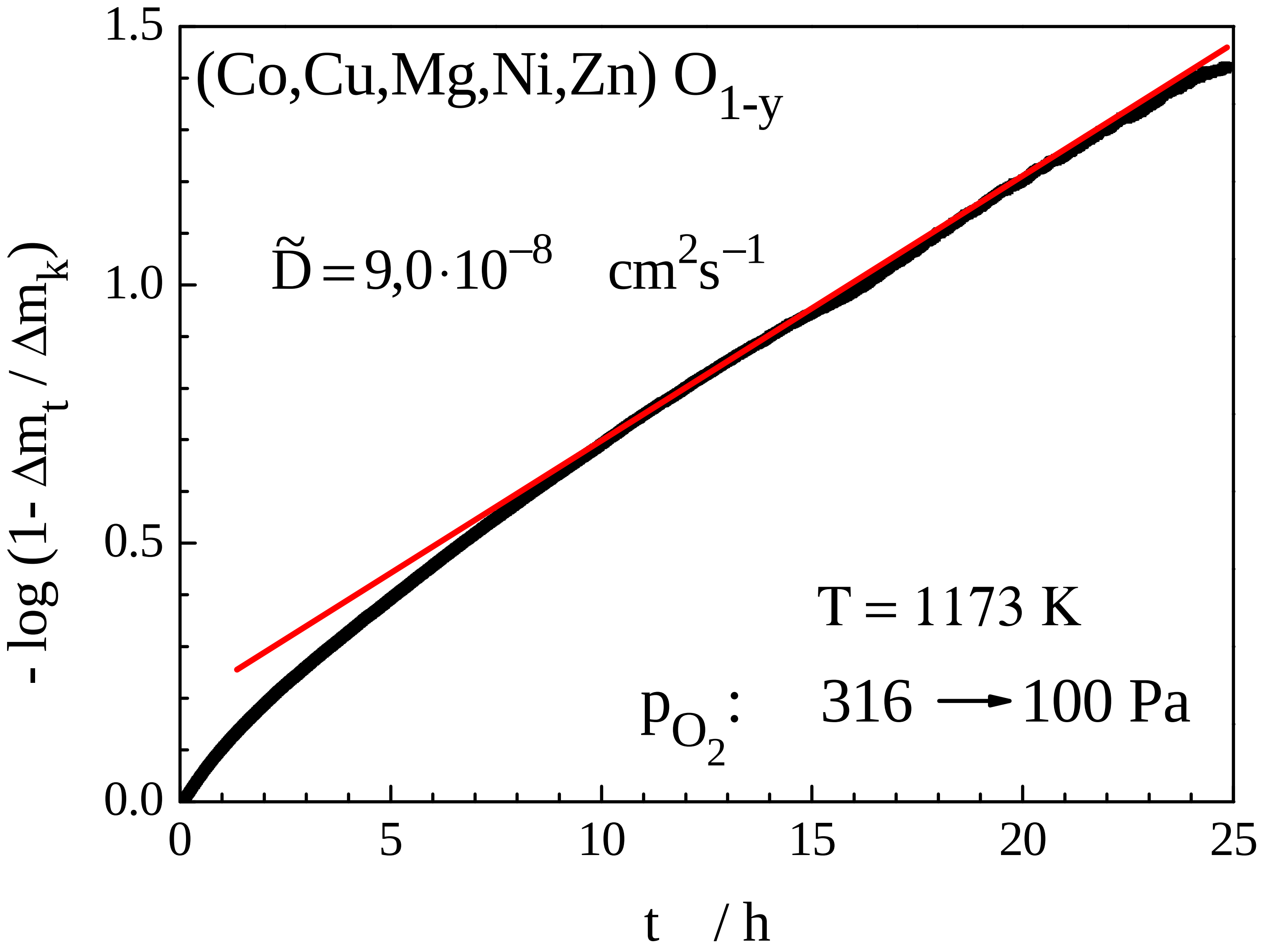
Initial reduction stage of (Co,Cu,Mg,Ni,Zn) O_{1-y}



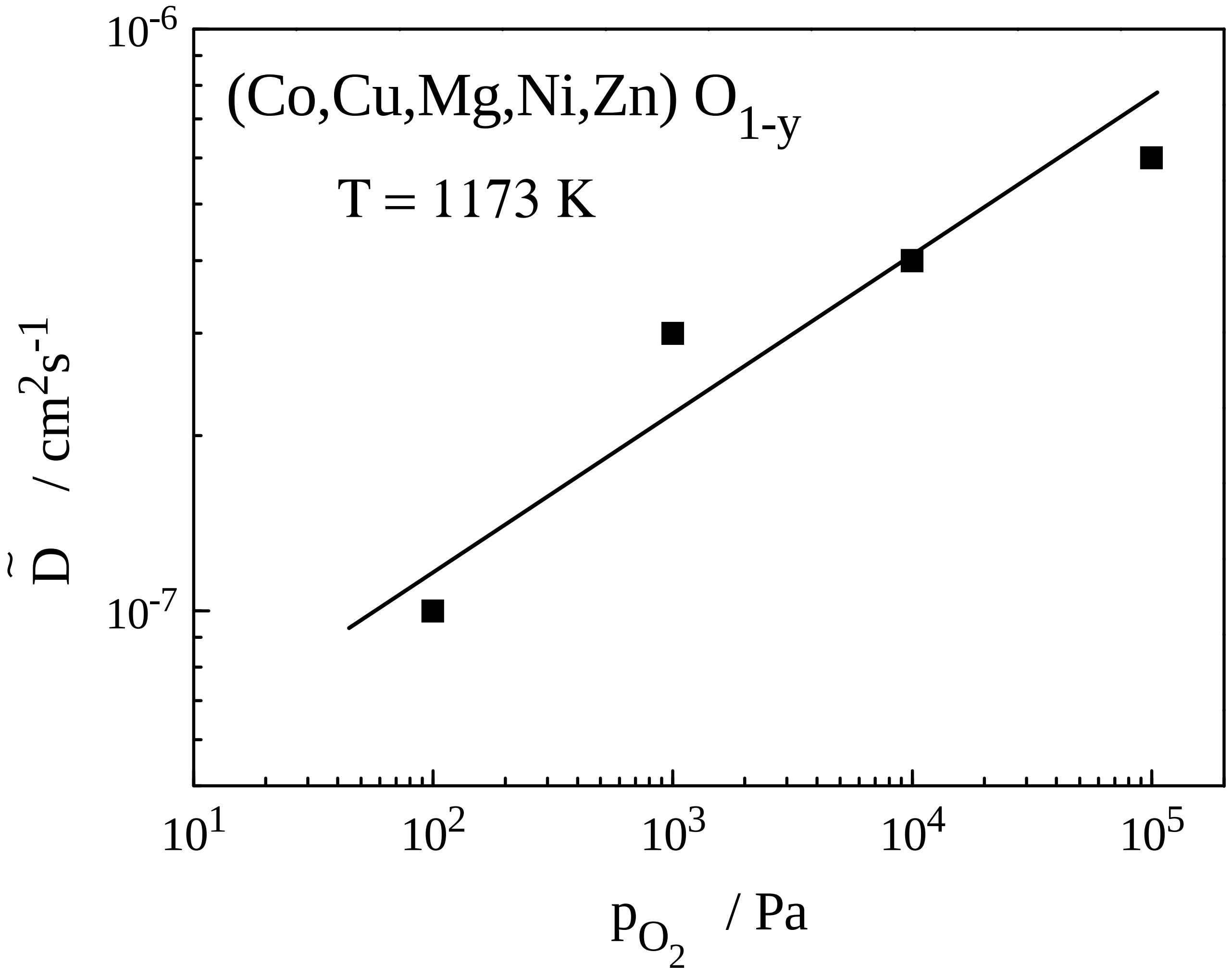
Re-equilibration kinetics of (Co,Cu,Mg,Ni,Zn) O_{1-y} illustrated in a parabolic system of coordinates



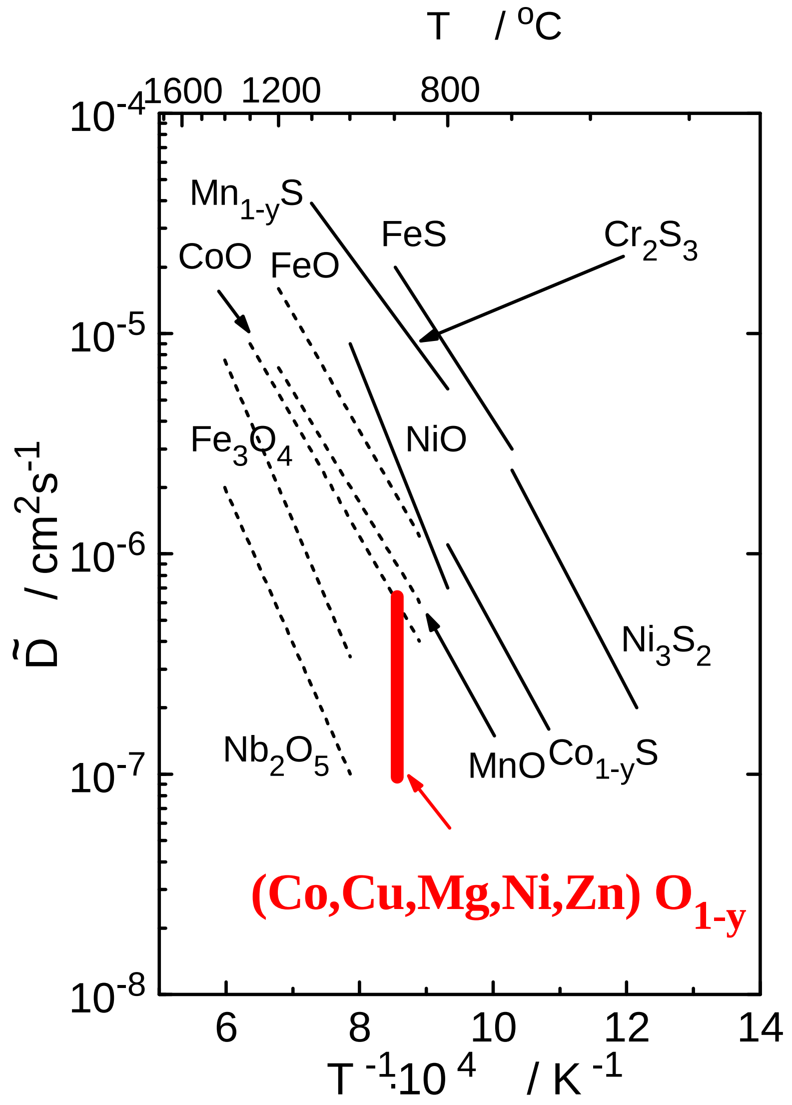
Re-equilibration kinetics of (Co,Cu,Mg,Ni,Zn) O_{1-y} illustrated in a semi-logarithmic system



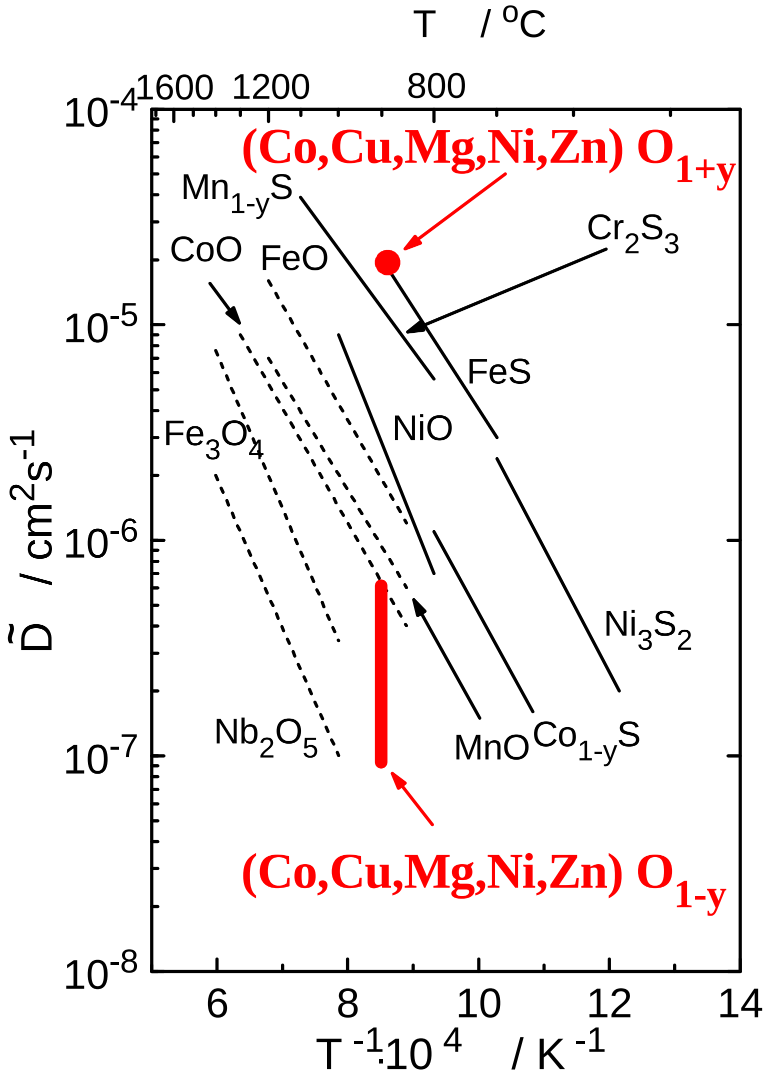
Correlation between the chemical diffusion coefficient in (Co,Cu,Mg,Ni,Zn) O_{1-y} and oxygen equilibrium pressure



Temperature dependence of chemical diffusion coefficients in selected metal oxides and sulphides



Temperature dependence of chemical diffusion coefficients in selected metal oxides and sulphides



Conclusions

1. In the thermodynamic conditions, under which (Co,Cu,Mg,Ni,Zn)O_{1-y} oxide was studied, it was determined that:

- predominant disorder is present in its anion sublattice,
- the predominant defects are anion vacancies,
- deviation from stoichiometry can assume large values ($y = 0{,}07$),
- the chemical diffusion coefficient is dependent on oxygen pressure ($10^{-7} – 6 \cdot 10^{-7}$ cm^2s^{-1}),

2. Large deviation from stoichiometry values and the oxygen pressure dependence of the chemical diffusion coefficient suggests a complex defect structure inside the studied oxide.

THANK YOU FOR YOUR ATTENTION