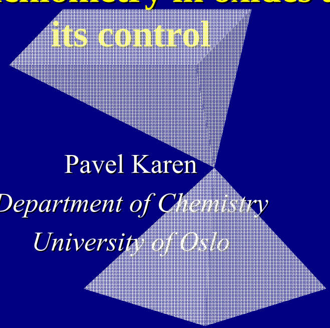
Nonstoichiometry in oxides and its control



Pavel Karen
Department of Chemistry
University of Oslo

Contents

Nonstoichiometry in ”stoichiometric” oxides

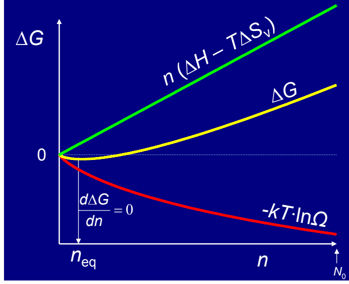
Al_2O_3

Alumina, after 1500°C in H_2; analytical composition $Al_2O_{2.97}$

Entropy favors defects

$N_0 + 1$

$$\Delta G = n(\Delta H - T\Delta S_v) - kT\ln\Omega$$



The number of possible permutations

$$\Omega = \frac{N!}{(N-n)!n!} \qquad \Omega = \frac{(N_0+n)!}{N_0!n!}$$

$$\Delta H - T\Delta S_v - kT\frac{d}{dn}\ln\frac{(N_0+n)!}{N_0!n!} = 0$$

$$\Delta H - T\Delta S_v - kT\cdot\ln\left(\frac{N_0+n_{eq}}{n_{eq}}\right) = 0$$

$$\frac{n_{eq}}{N_0+n_{eq}} = \exp\left(\frac{\Delta S_v}{k}\right)\cdot\exp\frac{-\Delta H}{kT}$$

Mass-action constant $K(T)$

Defects in pure Cr_2O_3

- Possible intrinsic defect reactions

Schottky: $2Cr_{Cr}^{\times} + 3O_O^{\times}$ nil $= 2v_{Cr}''' + 3v_O^{\bullet\bullet} + 2Cr_{Cr}^{\times} + 3O_O^{\times}$

Cation Frenkel: $Cr_{Cr}^{\times} = v_{Cr}''' + Cr_i^{\bullet\bullet\bullet}$

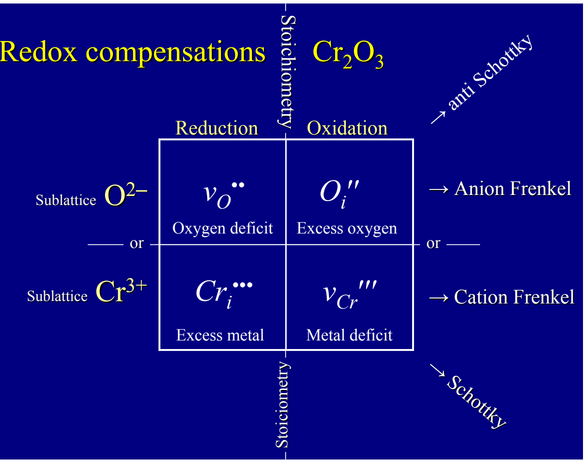
Anion Frenkel: $O_O^{\times} = v_O^{\bullet\bullet} + O_i''$

Intrinsic ionisation: $\mathrm{nil} = e' + h^{\bullet}$

$e' \rightarrow Cr_{Cr}'$ (Cr^{2+})

$h^{\bullet} \rightarrow Cr_{Cr}^{\bullet}$ (Cr^{4+})

Redox compensations Cr_2O_3



Schottky-type compensation

- Reduction

  $O_O^{\times} = 2e' + v_O^{\bullet\bullet} + 1/2\ O_{2(g)}$ $\qquad e' \rightarrow Cr_{Cr}'$ (Cr^{2+})

- Oxidation

  $3/2\ O_{2(g)} = 6h^{\bullet} + 2v_{Cr}''' + 3O_O^{\times}$ $\qquad h^{\bullet} \rightarrow Cr_{Cr}^{\bullet}$ (Cr^{4+})

Approximation adopted:

Vacancies are fully ionized

Approximation adopted

Concentrations of lattice sites =1 >> concentrations of defects

Defect equilibria

- Schottky $\qquad \mathrm{nil} = 2v_{Cr}''' + 3v_O^{\bullet\bullet} \qquad K_S = [v_{Cr}''']^2[v_O^{\bullet\bullet}]^3$
- Intrinsic ionization of electrons $\qquad \mathrm{nil} = e' + h^{\bullet} \qquad K_i = [e'][h^{\bullet}]$
- Oxidation $\qquad 3/2\ O_{2(g)} = 6h^{\bullet} + 2v_{Cr}''' + 3O_O^{\times} \qquad [v_{Cr}''']^2[h^{\bullet}]^6 = K_{ox}\cdot p_{O_2}^{3/2}$
- Reduction $\qquad O_O^{\times} = 2e' + v_O^{\bullet\bullet} + 1/2\ O_{2(g)} \qquad [v_O^{\bullet\bullet}][e']^2 = K_{red}\cdot p_{O_2}^{-1/2}$
- Electroneutrality condition $\qquad 3[v_{Cr}'''] + [e'] = [h^{\bullet}] + 2[v_O^{\bullet\bullet}]$

$$K_S\cdot K_i^6 = K_{ox}\cdot K_{red}^3$$

Defect concentrations as a function of p_{O_2}, with K_S, K_i, K_{ox} as parameters

$$2[h^{\bullet}]^5(K_S/K_{ox})^{1/3}p_{O_2}^{-1/2} + [h^{\bullet}]^4 - K_i[h^{\bullet}]^2 - 3K_{ox}^{1/2}p_{O_2}^{3/4} = 0$$

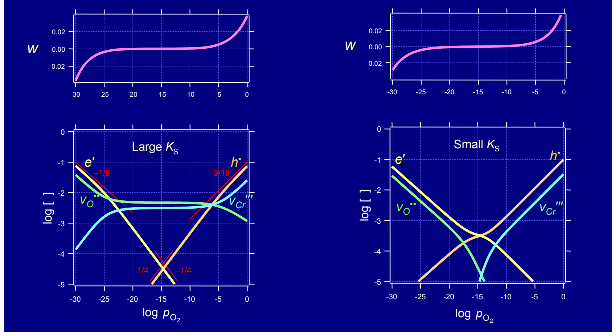
$$3[v_{Cr}''']^{5/3} + [v_{Cr}''']K_iK_{ox}^{-1/6}p_{O2}^{-1/4} - [v_{Cr}''']^{1/3}K_{ox}^{1/6}p_{O_2}^{1/4} - 2K_S^{1/3} = 0$$

$$3[e']^5(K_{ox}^{1/2}/K_i^3)p_{O_2}^{3/4} + [e']^3 - K_i[e'] - 2(K_s/K_{ox})^{1/3}K_ip_{O_2}^{-1/2} = 0$$

$$2[v_O^{\bullet\bullet}]^{5/2} + [v_O^{\bullet\bullet}]^2(K_{ox}/K_S)^{1/6}p_{O_2}^{1/4} - K_i[v_O^{\bullet\bullet}](K_S/K_{ox})^{1/6}p_{O_2}^{-1/4} - 3K_S^{1/2} = 0$$

Cr_2O_{3+w} $w=(3/2)[v_{Cr}''']-[v_O^{\bullet\bullet}]$

Defect concentrations

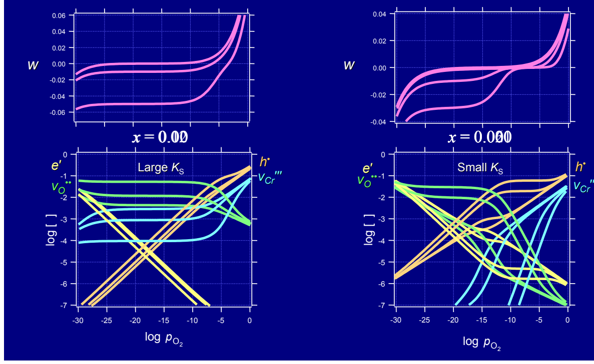


Acceptor doping; $Cr_{2-x}Mg_xO_{3+w}$

- Schottky $\quad nil = 2v_{Cr}''' + 3v_O^{\bullet\bullet} \quad K_S = [v_{Cr}''']^2[v_O^{\bullet\bullet}]^3$
- Intrinsic ionization of electrons $\quad nil = e' + h^\bullet \quad K_i = [e'][h^\bullet]$
- Oxidation $\quad 3/2\ O_2(g) = 6h^\bullet + 2v_{Cr}''' + 3O_O^x \quad [v_{Cr}''']^2[h^\bullet]^6 = K_{ox} p_{O_2}^{3/2}$
- Reduction $\quad O_O^x = 2e' + v_O^{\bullet\bullet} + 1/2\ O_2(g) \quad [v_O^{\bullet\bullet}][e']^2 = K_{red} p_{O_2}^{-1/2}$
- Electroneutrality condition $\quad 3[v_{Cr}''']+[e'] + [Mg_{Cr}'] = [h^\bullet]+2[v_O^{\bullet\bullet}]$

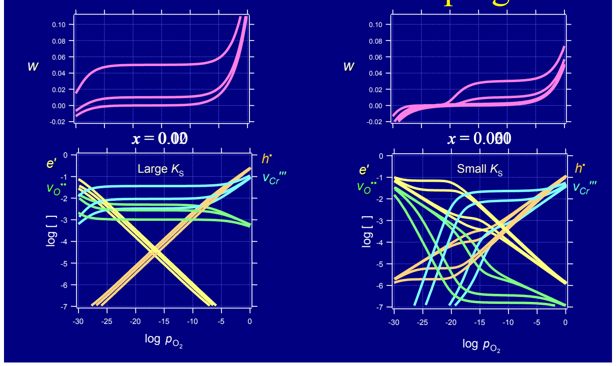
$Cr_{2-x}Mg_xO_{3+w}$ $w=(3/2)[v_{Cr}''']-[v_O^{\bullet\bullet}]$

Defect concentrations



$Cr_{2-x}Ti_xO_{3+w}$ $w=(3/2)[v_{Cr}''']-[v_O^{\bullet\bullet}]$

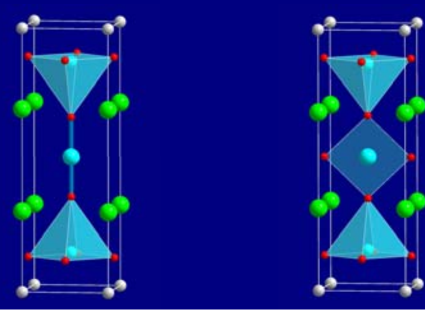
The same for donor doping



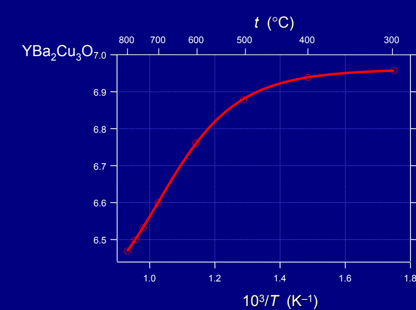
Continuous oxygen occupation between two limiting structural polyhedra

Wide range of nonstoichiometry

$YBa_2Cu_3O_6$ + ½ $O_2(g)$ = $YBa_2Cu_3O_7$

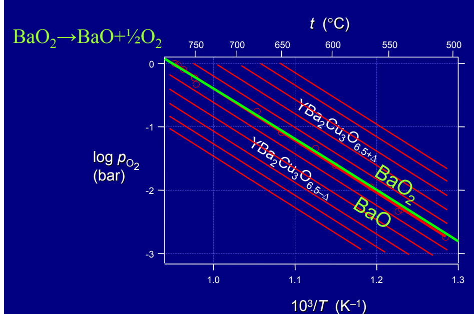


Constant O_2 pressure



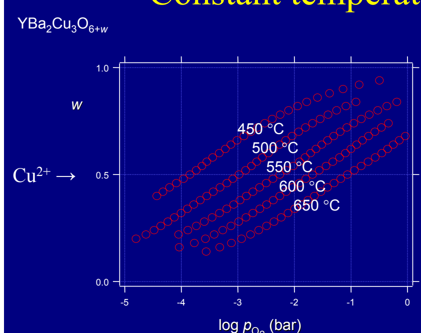
Fjellvåg, Karen, Kjekshus, Kofstad, Norby: *Acta Chem. Scand.* A42 (1988) 178

Constant composition; $YBa_2Cu_3O_{6.5}$



Fjellvåg, Karen, Kjekshus, Kofstad, Norby: *Acta Chem. Scand.* A42 (1988) 178

Constant temperature



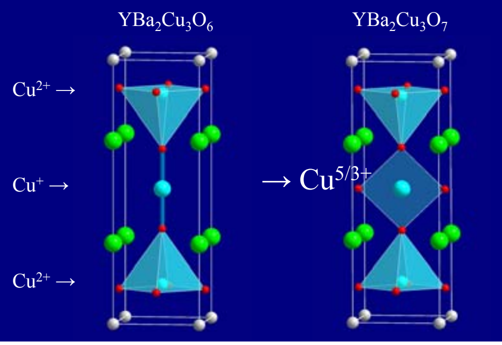
Cu^{2+} here does not represent any stoichiometric composition

Data: Schleger, Hardy, Yang: *Physica* C176 (1991) 261

Approaches

- Defect model as a doped oxide
  - Either $YBa_2Cu_3O_6$ or $YBa_2Cu_3O_7$
- Phenomenological defect models with defect clustering
- Lattice-gas model (thermodynamic approach)

Stoichiometric composition?



Doping the stoichiometric point

- $Y_3Cu_3^{5/3+}O_7$ acceptor-doped with 2Ba

  Doping defines an oxygen-content change between:
  - Integer-valence composition (when $e' = h^{\bullet}$), and
  - Integer-structure composition

  Just like for $Cr_{2-x}Mg_xO_3$, between:
  - trivalent Cr (and some oxygen vacancies), and
  - the integer structure of the oxide with 3O per metal atom (and some tetravalent chromium)

Defects in pure $Y_3Cu_3^{5/3+}O_7$

- Intrinsic defect reactions

  Anion Frenkel: $O_O^{\times} = v_O^{\bullet\bullet} + O_i''$

  Intrinsic ionisation: nil $= e' + h^{\bullet}$

$[Ba_Y']=2$

Acc. Doping: $Y_{3-2}Ba_2Cu_3^{5/3+}O_7$

- Anion Frenkel $O_O^{\times} = v_O^{\bullet\bullet} + O_i''$ $K_F = [v_O^{\bullet\bullet}][O_i'']$
- Intrinsic ionization of electrons nil $= e' + h^{\bullet}$ $K_i = [e'][h^{\bullet}]$
- Oxidation $\frac{1}{2}O_{2(g)} = 2h^{\bullet} + O_i''$ $[O_i''][h^{\bullet}]^2 = K_{ox} \cdot p_{O_2}^{1/2}$
- Reduction $O_O^{\times} = 2e' + v_O^{\bullet\bullet} + \frac{1}{2}O_{2(g)}$ $[v_O^{\bullet\bullet}][e']^2 = K_{red} \cdot p_{O_2}^{-1/2}$
- Electroneutrality condition $2 + 2[O_i''] + [e'] = [h^{\bullet}] + 2[v_O^{\bullet\bullet}]$

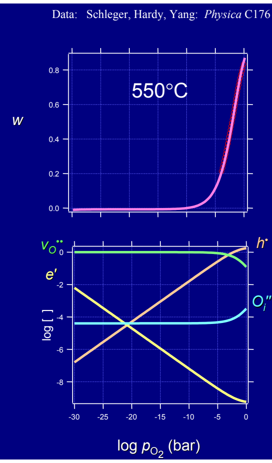
$K_F \cdot K_i^2 = K_{ox} \cdot K_{red}$

Data: Schleger, Hardy, Yang: *Physica* C176 (1991) 261

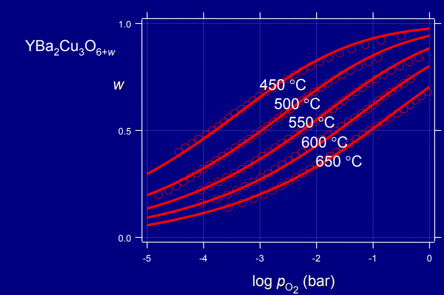
"Defect" concentrations

$K_{ox} = 10^{-3}$
$K_i = 10^{-9}$
$K_F = 4 \cdot 10^{-5}$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$



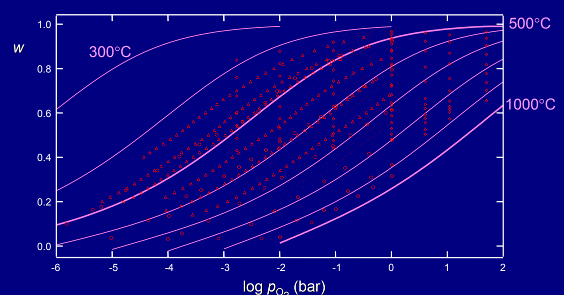
Temperature dependence



Data: Schleger, Hardy, Yang: *Physica* C176 (1991) 261

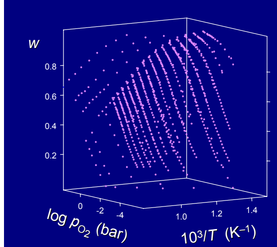
Data: Schleger, Hardy, Yang: *Physica* C176 (1991) 261 Meuffels, Naeven, Wenzl: *Physica* C161 (1989) 539
Matthews, Jacob: *Metall. Trans.* A23 (1992) 3325 Conder, Karpinski, Kaldis, Rusiecki, Jilek: *Physica* C196 (1992) 164

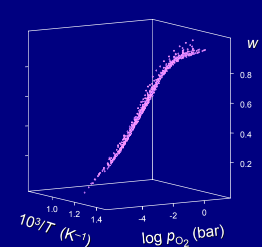
… of more data



Karen, Kjekshus: **Phase diagrams and thermodynamic properties,** *Handbook on the Physics and Chemistry of Rare Earths* 30 (2000) 229–373

One more look at the raw data



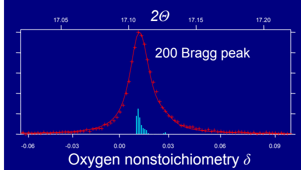


Oxygen engineering

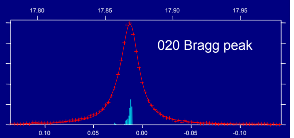
- Control of the overall oxygen content
- Control of its distribution
- Evaluation of the distribution

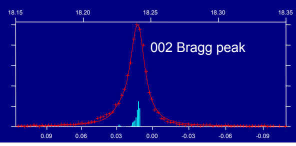
Karen: J. Solid State Chem. 170 (2003) 9

Oxygen content distribution



An orthorhombic perovskite



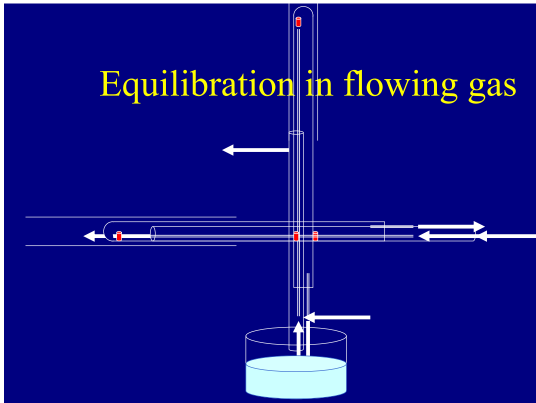


Oxygen-content distribution that fits the three peaks

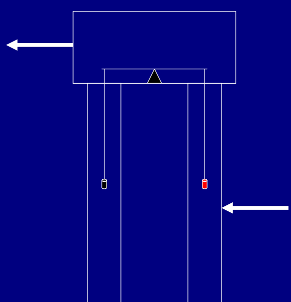
Control of oxygen content

Control parameters	Redox reagens	System
T and p_{O_2}	flowing gas	open
mass, T	flowing gas	open
T	p_{O_2} buffer	closed
mass (n_{O_2})	oxygen getter	closed

Equilibration in flowing gas

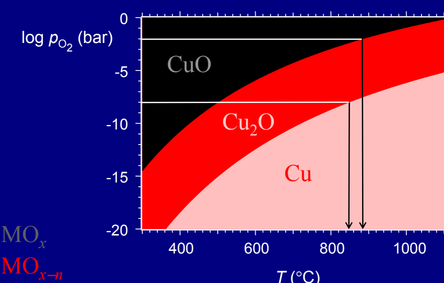


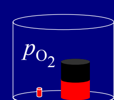
Equilibration in a thermobalance



Karen, Braaten, Fjellvaag, Kjekshus: NASA Conference Publication (1991), 3100(AMSAHTS '90), 117

Equilibration with p_{O_2} buffer



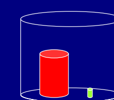


MO_x

MO_{x-n}

$n = ½…x$

Equilibration with p_{O_2} getter



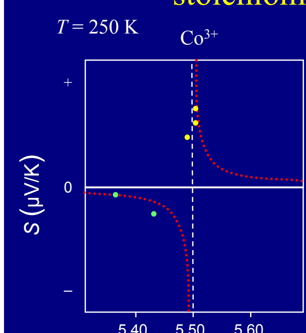
$n\mathrm{MO}_{i+\Delta i} + n\Delta i/2\ \mathrm{Zr} \rightarrow n\mathrm{MO}_i + n\Delta i/2\ \mathrm{ZrO_2}$

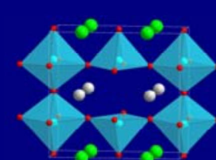
Properties that are very sensitive to the oxygen nonstoichiometry

- Properties that change abruptly at the stoichiometric point
- Properties related to valence mixing

Unpublished: Okamoto: Tokyo Institute of Technology

Seebeck coefficient at the stoichiometric point





$NdBaCo_2^{III}O_{5.50}$

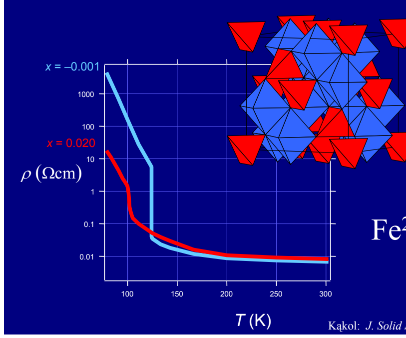
1. Uncertainty in doping level?

or

2. Higher mobility of $h^\bullet$ than e'

Crystal treatment: V.A.M. Brabers, Eindhoven University of Technology

Verwey transition in magnetite



$Fe^{2+}(Fe^{2+}Fe^{3+})O_{4+x}$

Kąkol: J. Solid State Chem. 88 (1990) 104