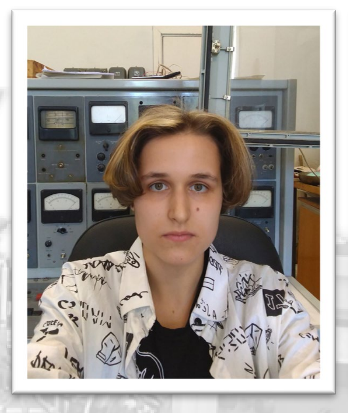
THERMODYNAMIC PROPERTIES OF THE CeO_2-Gd_2O_3 SYSTEM

O.A. Zhinkina, S.M. Shugurov, E.A. Balabanova, D.A.Repin, S.I. Lopatin
st107449@student.spbu.ru



Introduction

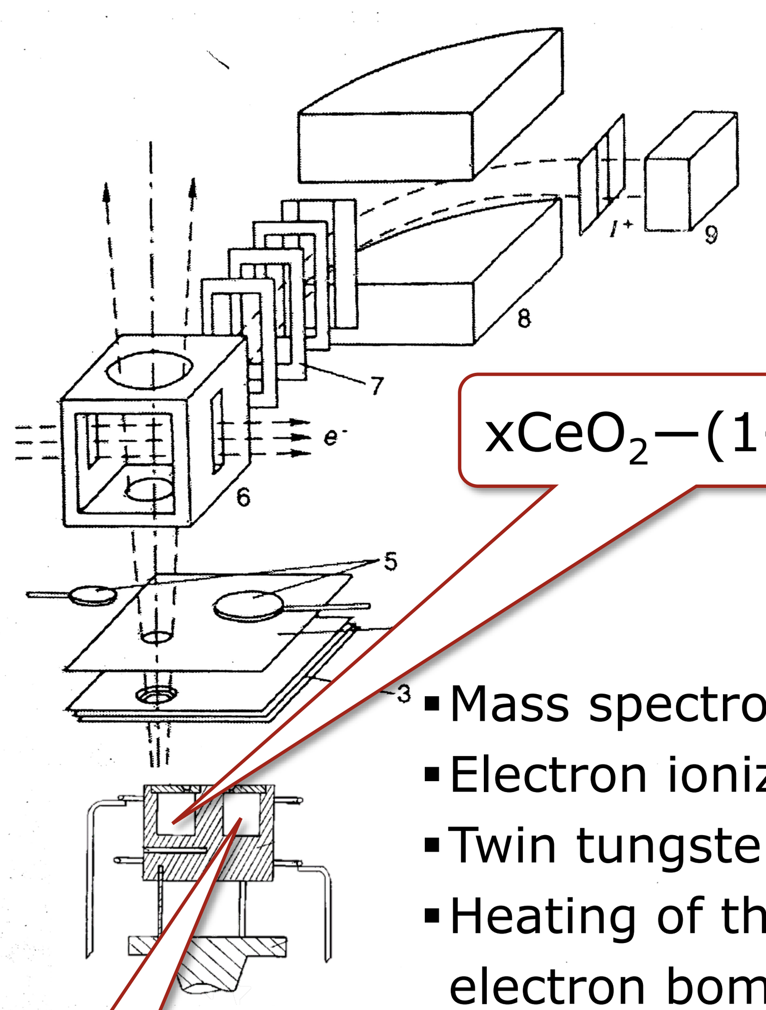
Rare earth-doped ceria has been the subject of thorough research as an electrolyte for solid oxide fuel cells (SOFC) due to its exceptional ionic conductivity. Gd-doped ceria (GDC) has demonstrated superior performance in this field compared to the frequently utilized Y-stabilized zirconia (YSZ).

Elevated temperatures during the process of synthesis and application could potentially result in the selective evaporation of the components in the examined system. The knowledge of vapour composition as well as thermodynamic properties of the system is useful to predict the behavior of material in such conditions.

Objective

Investigation of vaporization processes and thermodynamic properties of the CeO_2-Gd_2O_3 system

KEMS method



- Mass spectrometer MS-1301
- Electron ionization, 30 эВ
- Twin tungsten effusion cell
- Heating of the cell – electron bombardment
- Optical pyrometer EOP-66

Main equations

Relation between pressure and ionization current:

$$p = \frac{k}{\sigma} IT$$

(k/σ is constant for a specie during one experiment)

Activities:

$$a(CeO_2) = \frac{p(CeO_2)}{p^{\circ}(CeO_2)} = \frac{I(CeO_2)}{I^{\circ}(CeO_2)}$$

$$\ln a(Gd_2O_3) = - \int_{x(Gd_2O_3)=1}^{x(Gd_2O_3)=x} \frac{x(CeO_2)}{x(Gd_2O_3)} d \ln a(CeO_2)$$

Thermodynamic functions:

$$\Delta G^m = \sum_i x_i \Delta\mu_i^m = RT \sum_i x_i \ln a_i$$

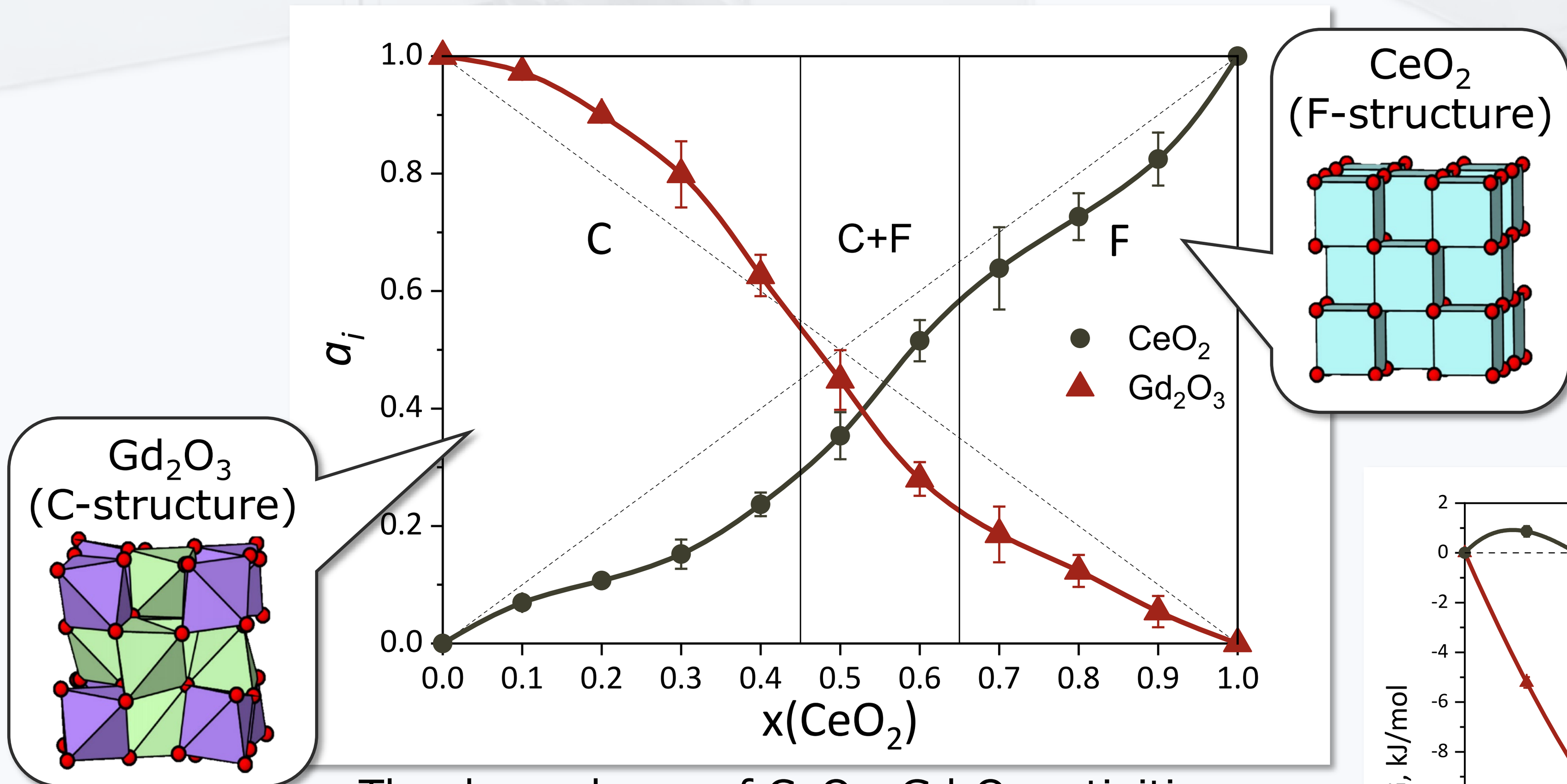
$$\Delta G^E = \sum_i x_i \Delta\mu_i^E = RT \sum_i x_i \ln \gamma_i$$

$$\left(\frac{\partial \ln a_i}{\partial 1/T}\right)_{p,x_i} = \frac{\Delta H_i^m}{R}$$

Synthesis

Solid state synthesis:
$Ce_{1-x}Gd_xO_{2-x/2}$
(x=0.1 to 0.9 at 0.1 intervals)
T=1400°C
48h

Results

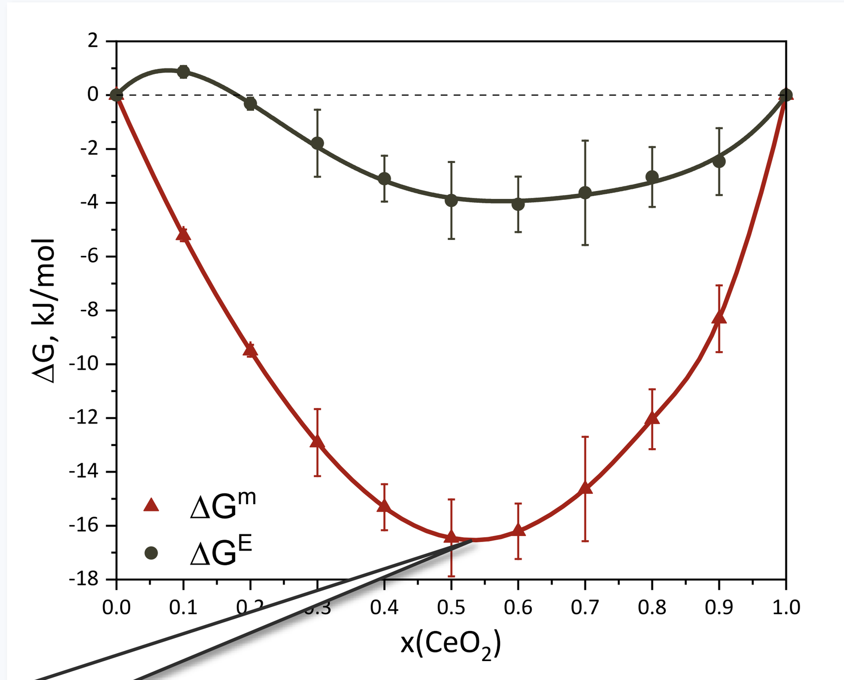


The dependence of CeO_2, Gd_2O_3 activities on ceria mole fraction at 2150 K with different structure solid solution boundaries[1]

Vapour composition

Ion (m/z)	Molecule
CeO^+(156)	CeO, CeO_2
CeO_2^+(172)	CeO_2
GdO^+(176)	GdO

$CeO+e^-=CeO^++2e^-$
$CeO_2+e^-=CeO_2^++2e^-$
$CeO_2+e^-=CeO^++O+2e^-$



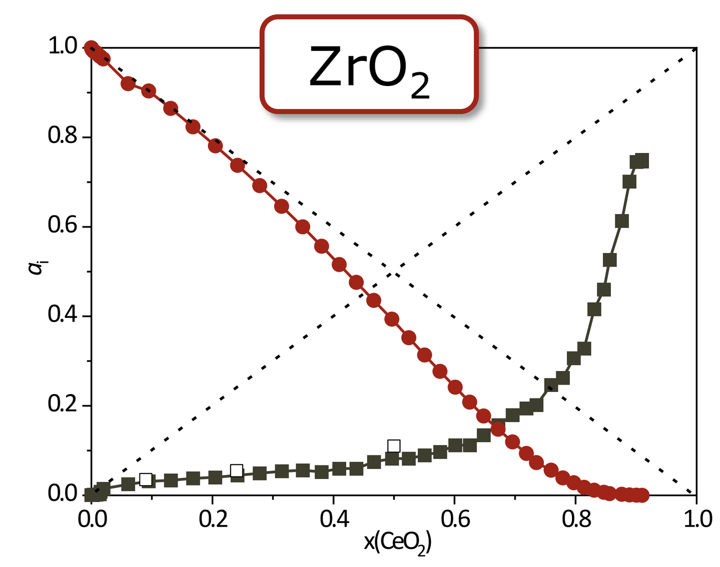
The dependence of ΔG^m and ΔG^E on ceria mole fraction at 2150 K

Activities do not depend on temperature:

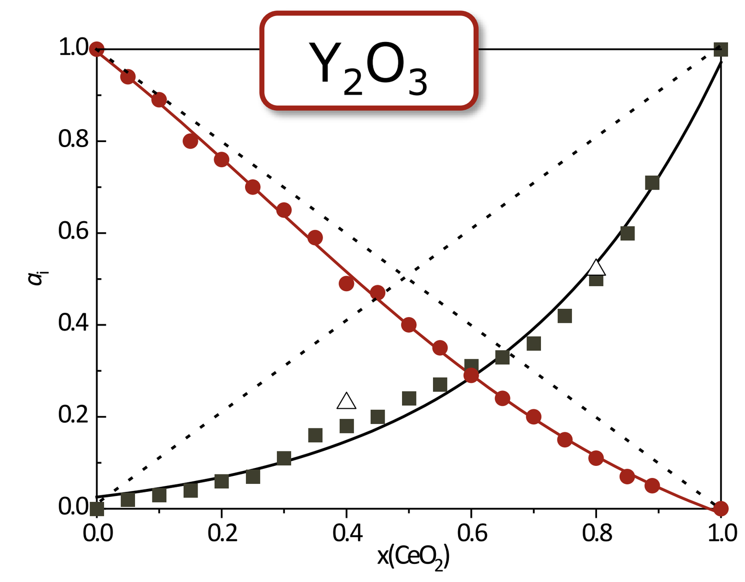
$$\Delta H_i^m \approx 0$$

ΔG^m minimum
x(CeO_2)=0.53
(-16.5±1.4) kJ/mol

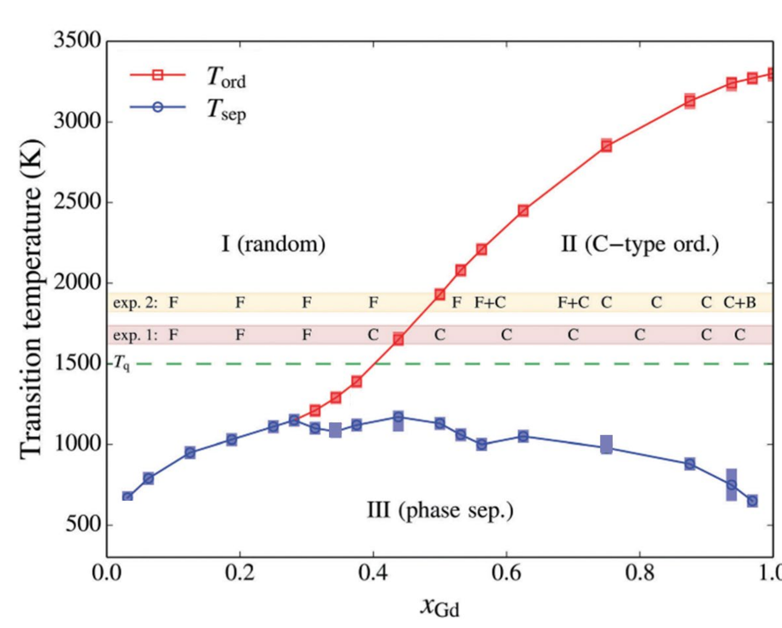
Literature review



The dependence of CeO_2 (black), ZrO_2 (red) activities on ceria mole fraction[2]



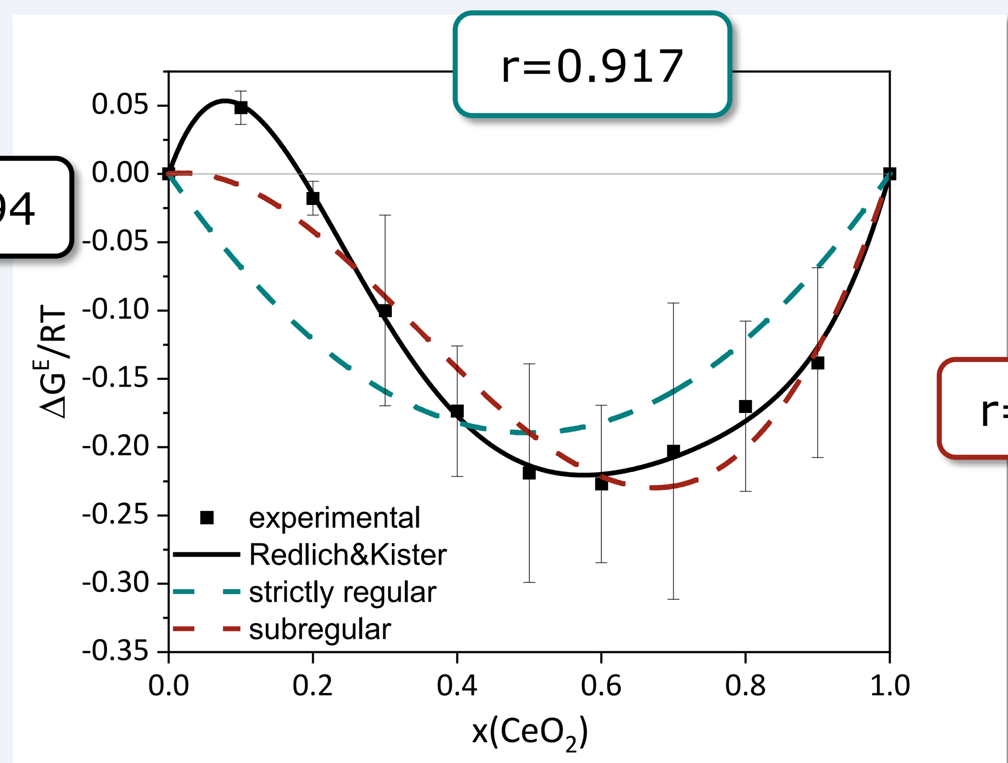
The dependence of activities CeO_2 (black), Y_2O_3 (red) on ceria mole fraction[3]



Theoretical phase diagram of the CeO_2-Gd_2O_3 system compared to experimental results[4]

Conclusions

The approximation of experimental results

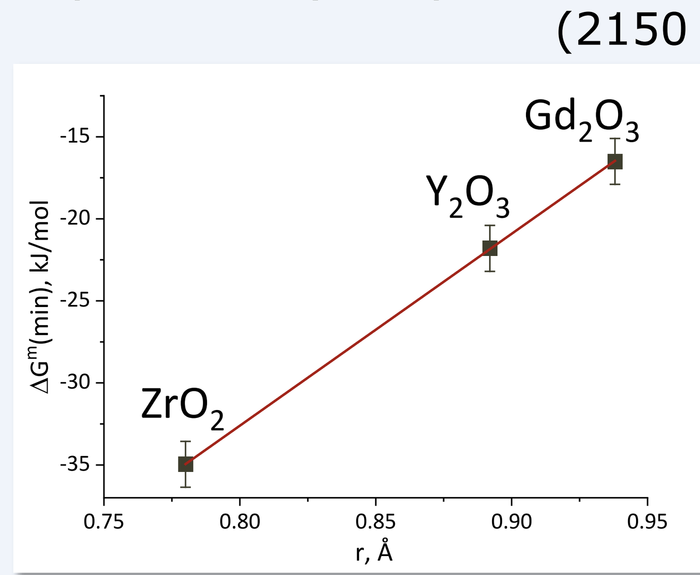


$\Delta G^E = A x_1 x_2$ Strictly regular

$\Delta G^E = (A_1 x_1 + A_2 x_2) x_1 x_2$ Subregular

$\Delta G^E = RT x_1 x_2 \sum_0^3 C_n (x_1 - x_2)^n$ Redlich&Kister

Comparison with similar CeO_2-containing systems: the possibility to predict thermodynamic properties (2150 K)



ΔG^m_{min} – is the value of minimum ΔG^m in the system

r – is the Shannon ionic radii of the second component

$$\Delta G^m_{min}[kJ/mol] = (116.96 \pm 0.51) r[Å] - 126.17 \pm 0.45$$

References:
[1]Handbook on the Phys. and Chem. of Rare Earths. 1979. Vol. 3. P. 401–524
[2]J. Alloys Compd. 2019. Vol. 776. P. 194–201
[3]Ceram. Int. 2021. Vol. 47, № 8. P. 11072–11079
[4]Phys. Chem. Chem. Phys. 2018. Vol. 20, № 17. P. 11805–11818

Acknowledgments: The financial support of Russian science foundation (24-23-00047). Authors are grateful to Cryogenic department and Center for X-ray Diffraction Studies of the Science Park of St. Petersburg State University