Serbian Ceramic Society Conference
ADVANCED CERAMICS AND APPLICATION IV

Serbian Academy of Sciences and Arts, Knez Mihailova 35
Serbia, Belgrade,
21-23. September 2015

THERMAL TREATMENT OF OXIDES IN DIFFERENT ATMOSPHERES

Nebojša Labus[1], Zorka Z. Vasiljević[1], Slavko Mentus[2,3], Vladimir B. Pavlović[1], Miloljub Luković[4], Maria Vesna Nikolić[4]

[1]Institute of Technical Sciences of SASA, Knez 35, 11000 Belgrade, Serbia

[2]Faculty of Physical Chemistry, Studenski trg 12-16, 11158 Belgrade, University of

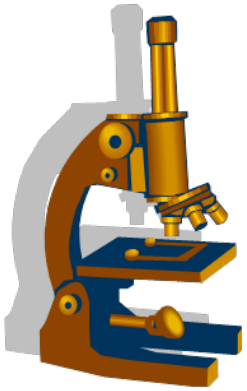
Belgrade, Serbia

[3]Serbian Academy of Sciences and Arts, Knez Mihailova 35, 11000 Belgrade, Serbia

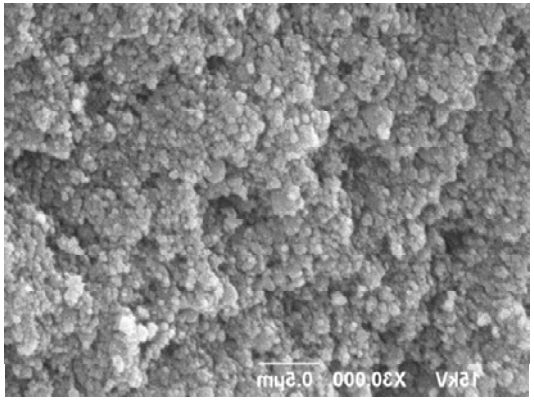
[4]Institute for Multidisciplinary Research, Kneza Višeslava 1, 11000 Belgrade, University of Belgrade, Serbia

Aim

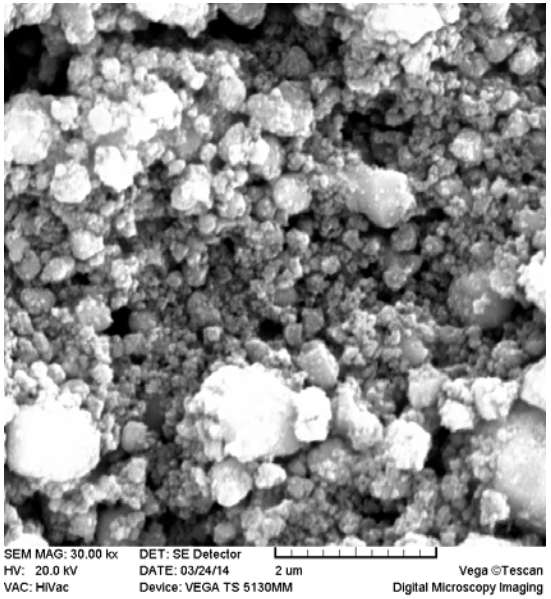
TiO_2 nanopowder,
Alfa Aesar 99.7%
anatase with sizes of
particles from
10 nm to 15 nm

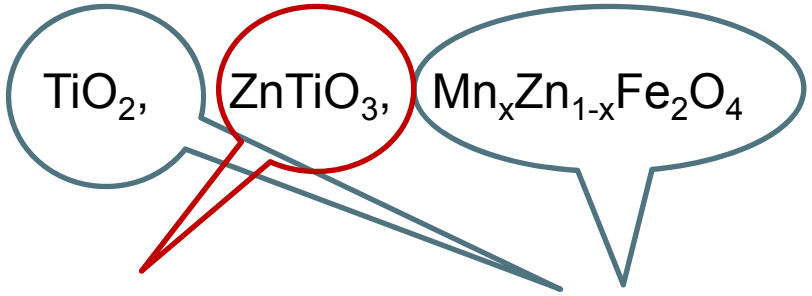


$ZnTiO_3$ nanopowder,
Aldrich
[CAS 112036-43-0]



Comercial ,
Micro powder
Composition:
$Mn_{0.63}Zn_{0.37}Fe_2O_4$, 93 wt.%
and Fe_2O_3 7 wt.%

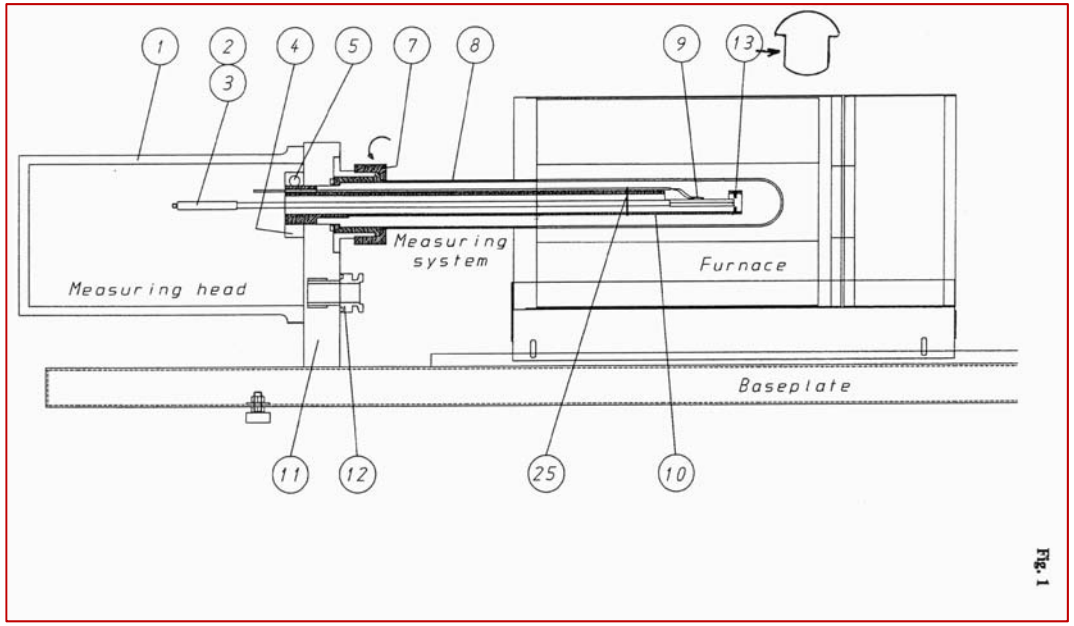




Stoichiometric - nonstoichiometric
compounds

15 nm 30 nm >1μm

Technical approach



Gas chamber in the dilatometric device and vacuum and atmosphere exits

Vacuum gauge

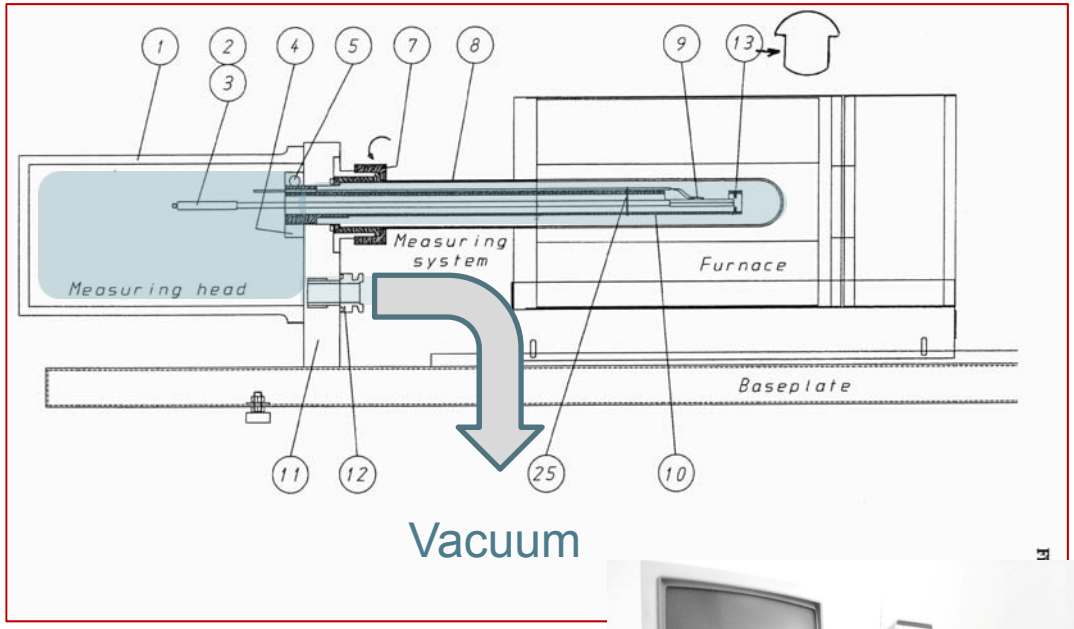
Main pressure valve

Manometer

Flow meter

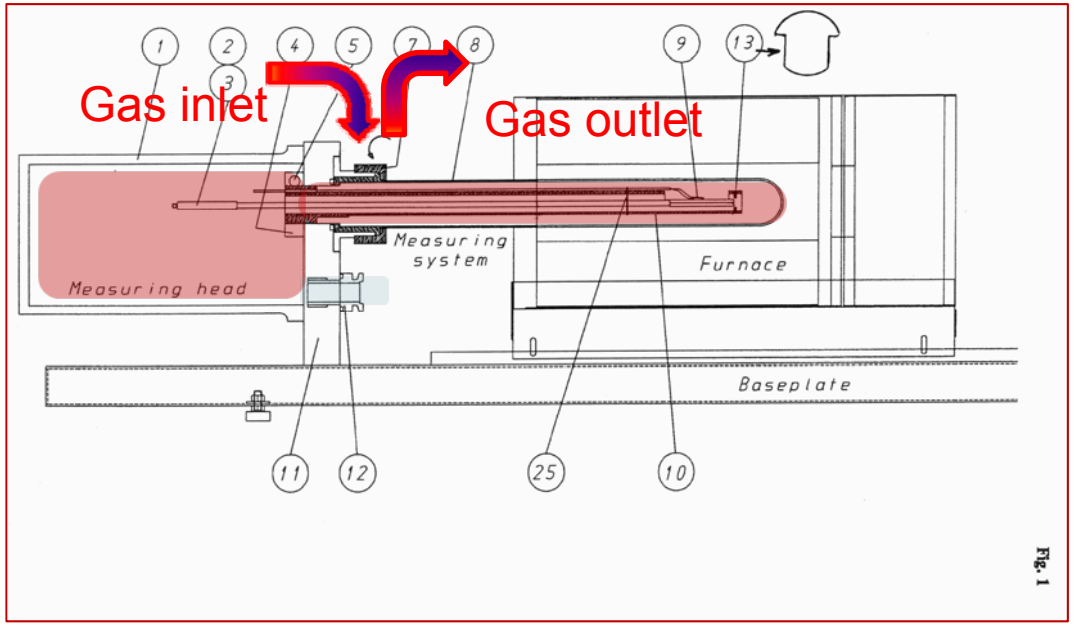
Gas inlet and outlet switches

Atmosphere regulation control unit



Gas chamber in the dilatometric device and vacuum and atmosphere exits

Equipment for the evacuating gas chamber in the dilatometric device



Gas chamber in the dilatometric device and vacuum and atmosphere exits

Theory - about point defects

Pergamon

PII: S0022-3697(97)00205-9

J Phys Chem Solids Vol 59, No. 4, pp 507–525, 1998

0022–3697/98 $19.00 + 0.00

POINT DEFECTS AND TRANSPORT IN NON-STOICHIOMETRIC OXIDES: SOLVED AND UNSOLVED PROBLEMS

RÜDIGER DIECKMANN

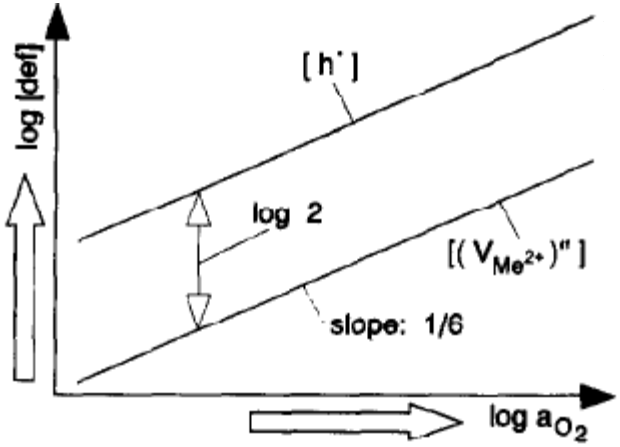


Fig. 3. Schematic plot of the concentrations of cation vacancies, $[(V_{Me^{2+}})'']$, and of holes, $[h^{\cdot}]$, in a model oxide of the type $Me_{1-\Delta}O$ with cation vacancies and holes as the majority defects and very small point defect concentrations.

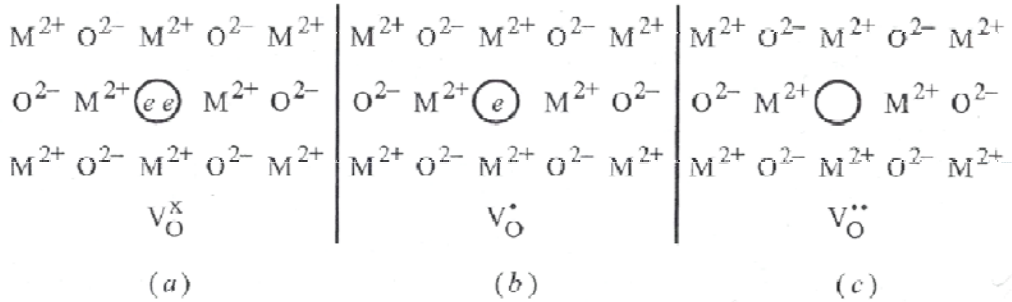
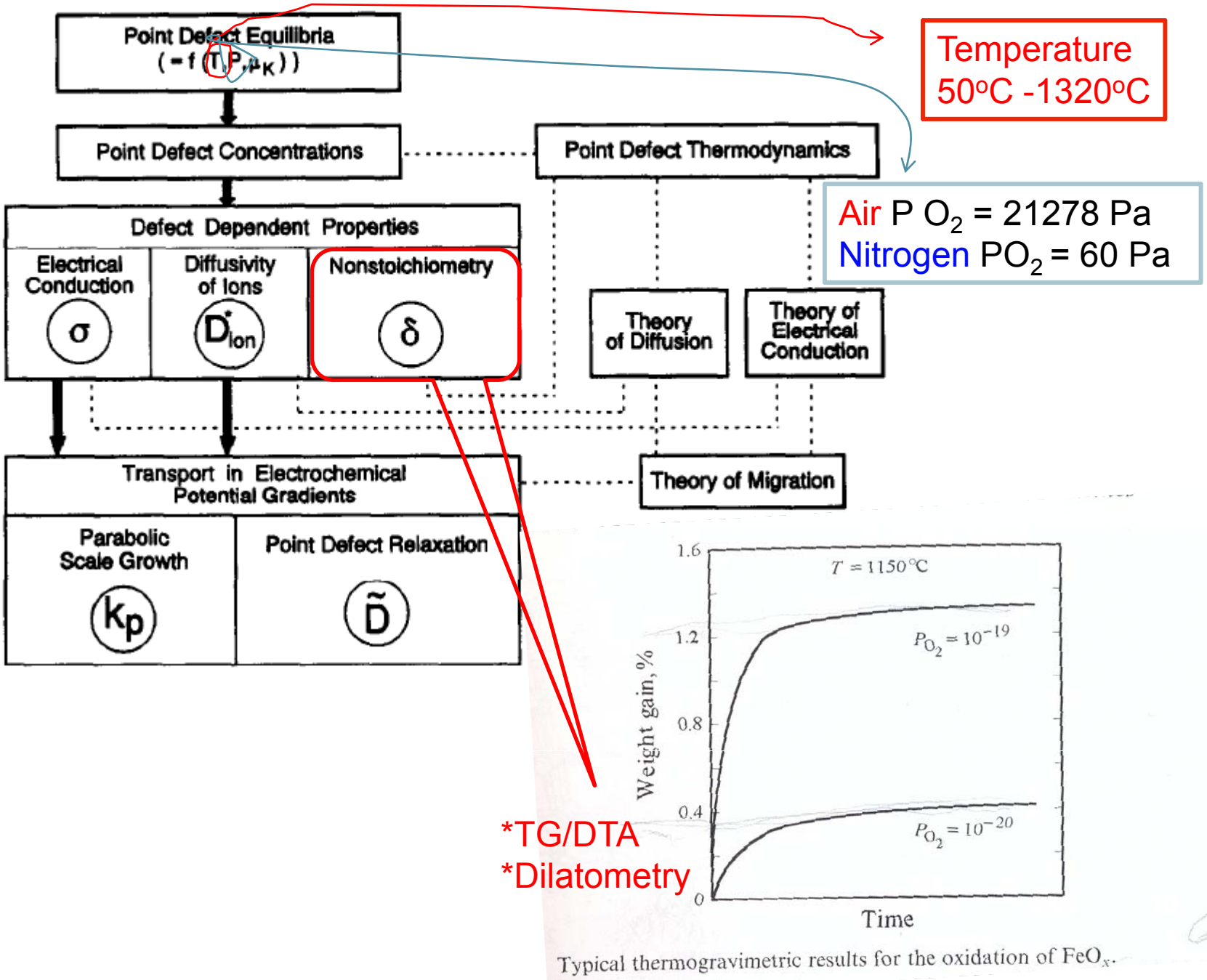


Figure 6.4 (*a*) The formation of an oxygen vacancy by the loss of an oxygen atom to the gas phase. This is a nonstoichiometric reaction because the crystal chemistry changes as a result. Note that as drawn, the electrons are localized at the vacancy site, rendering its effective charge zero. (*b*) A $V_O^{\bullet}$ site is formed when one of these electrons is excited into the conduction band. (*c*) The escape of the second electron creates a $V_O^{\bullet\bullet}$ site.



Typical thermogravimetric results for the oxidation of FeO_x.

TG determination of the non stoichiomtery

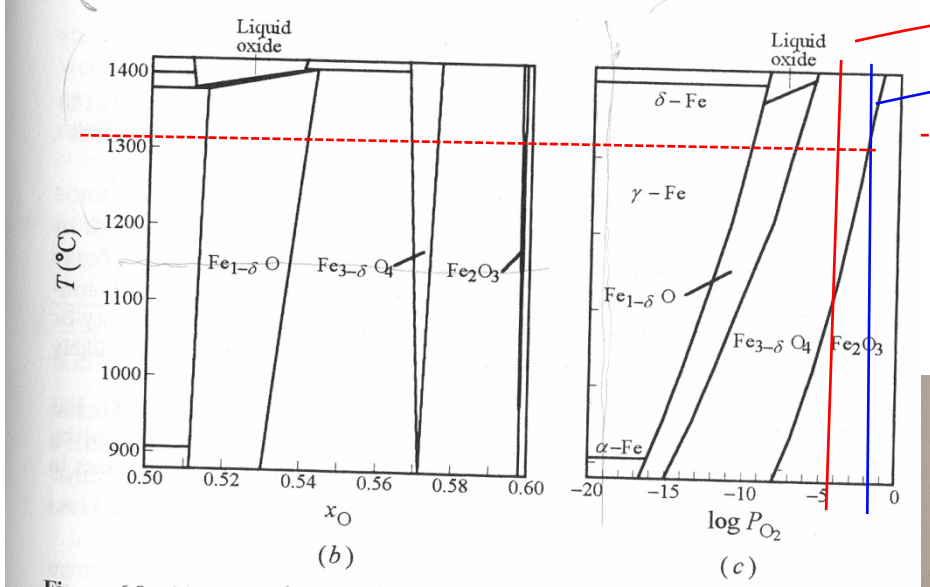


Figure 6.8 (*a*) Stability domains of various phases in the Mn-O system and the corresponding deviations in stoichiometry.[78] (*b*) Phase diagram of Fe-O system, x_O is mole fraction of oxygen, and (*c*) stability domains of the various phases in Fe-O system.[79]

Temperature
50°C -1320°C

Air pO_2 = 21278 Pa,
$-\log_{10} pO_2$ = 4.3279
Nitrogen pO_2 = 60 Pa
$-\log_{10} pO_2$ = 1.778

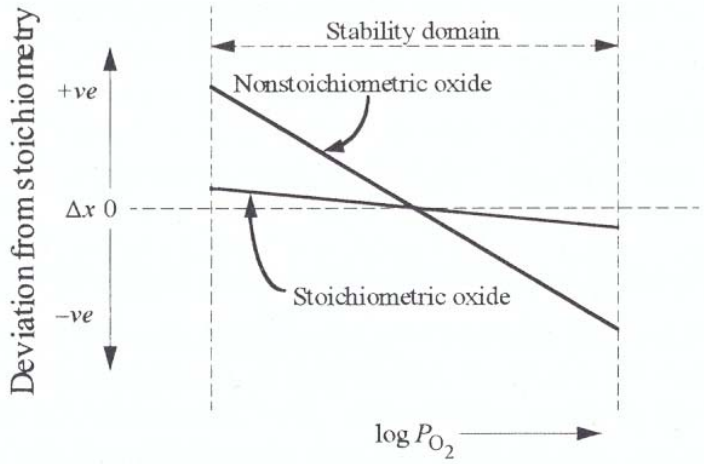
Table 6.1 Range of stoichiometry and existence domains of a number of binary oxides at 1000 K[77]

Oxides	Deviation from stoichiometry			Stability or existance region[‡] – log P_{O_2}	
	x_{min}	x_{max}	Δx[‡]	Min	Max
Nonstoichiometric oxides					
TiO	0.8	1.3	0.5	44.2[§]	41.5
Ti_2O_3	1.501	1.512	0.011	41.5	36.1
TiO_2	1.992	2.00	0.008	25.7	—
VO	0.8	1.3	0.5	35.9	33.2
MnO	1.00	1.18	0.18	34.5[§]	10.7
FeO	1.045	1.2	0.155	21.6[§]	17.9
Fe_3O_4	1.336	1.381	0.045	17.9	10.9
CoO	1.00	1.012	0.012	17.1[§]	2.5
NiO	1.00	1.001	0.001	16.5[§]	—
Cu_2O	0.500	0.5016	0.0016	9.97[§]	7.0
Stoichiometric oxides					
Al_2O_3	1.5000	1.5000		71.3	—
MgO	1.00000	1.0000		51.5	—

$$x = \frac{b}{a} \pm \delta$$

M_aO_b

TiO_2, b/a=2/1=2
x_{min}=1.992
x_{max}=2.00
Δx=0.008
$-\log P_{O2}$
Min=25.07
Max= /



Pergamon

PII: S0022-3697(97)00205-9

J Phys Chem Solids Vol 59, No. 4, pp 507–525, 1998

0022-3697/98 $19.00 + 0.00

POINT DEFECTS AND TRANSPORT IN NON-STOICHIOMETRIC OXIDES: SOLVED AND UNSOLVED PROBLEMS

RÜDIGER DIECKMANN

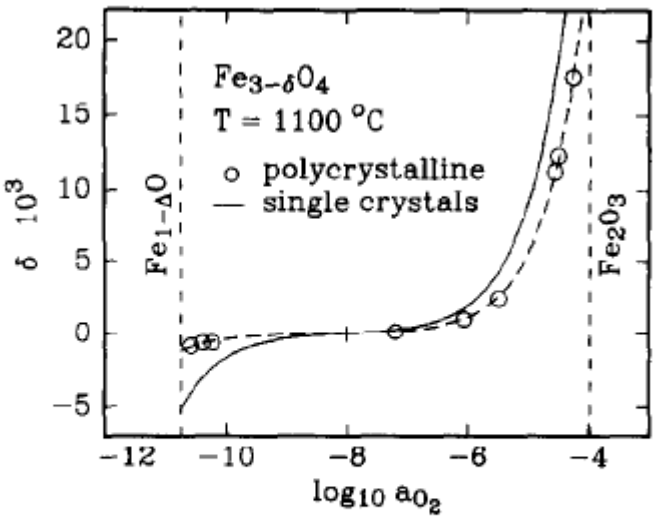


Fig. 19. Variation of δ in single-crystal and polycrystalline $Fe_{3-\delta}O_4$ at 1100°C.

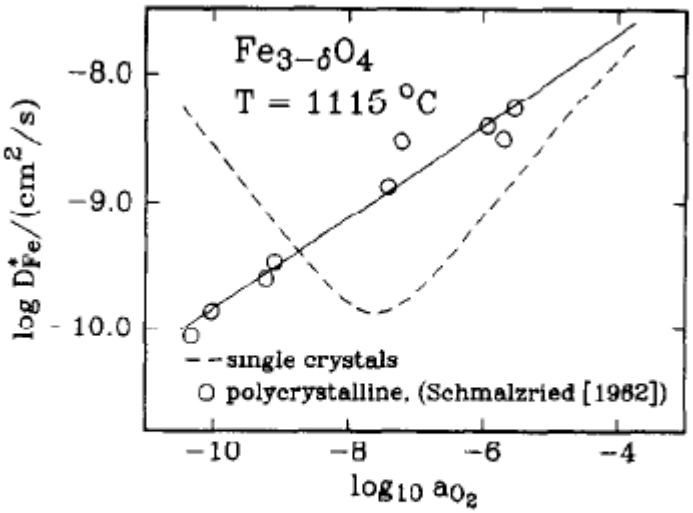
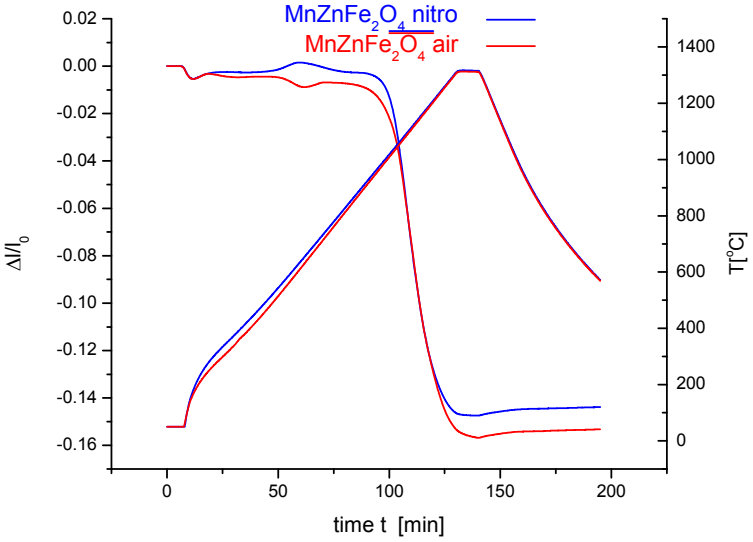
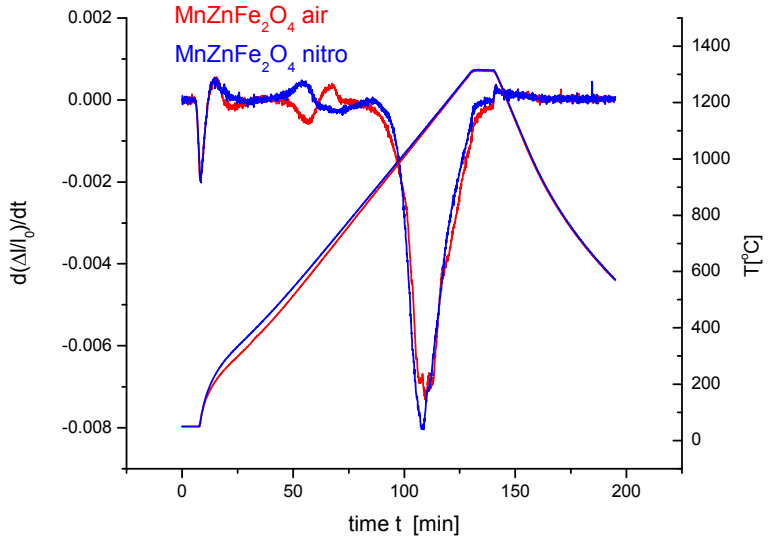


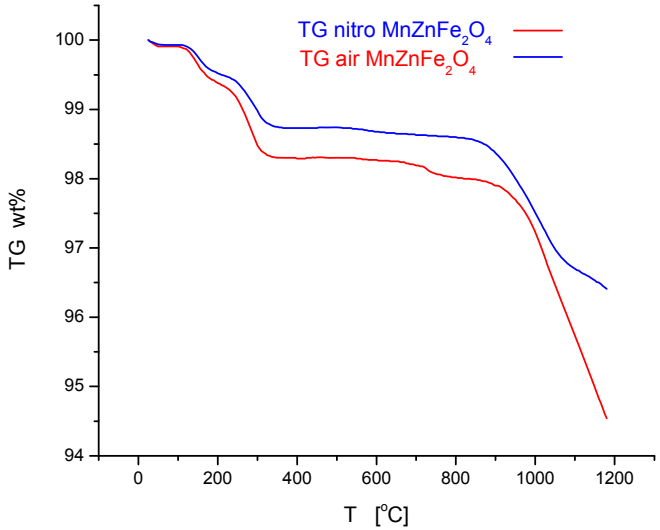
Fig. 20. Oxygen activity dependence of the iron tracer diffusion coefficient, D^*_{Fe}, in single-crystal and polycrystalline $Fe_{3-\delta}O_4$ [35] at 1115°C.

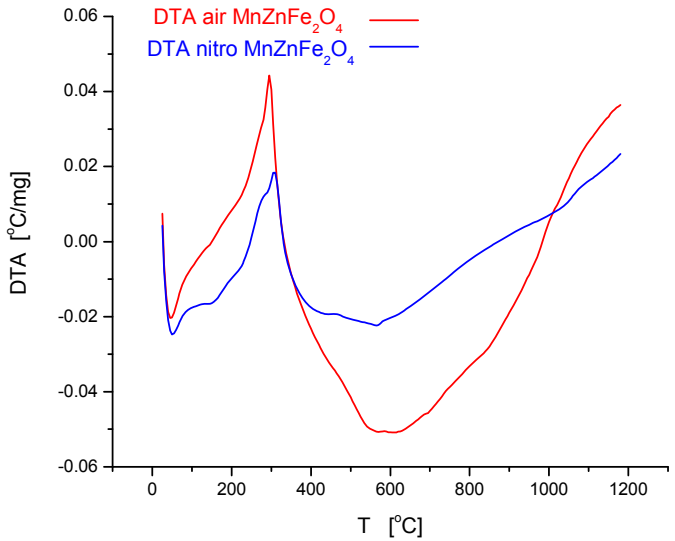
Results

Dilatometry and TG/DTA
$Mn_{1-x}Zn_xFe_2O_4$

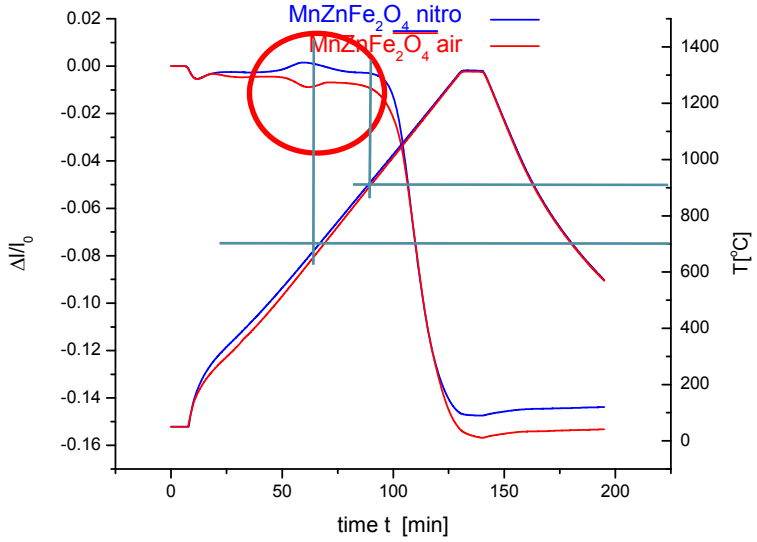


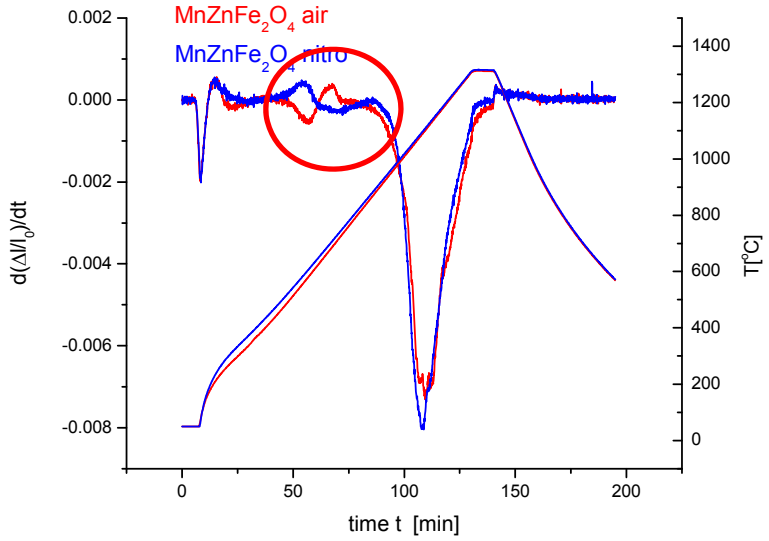


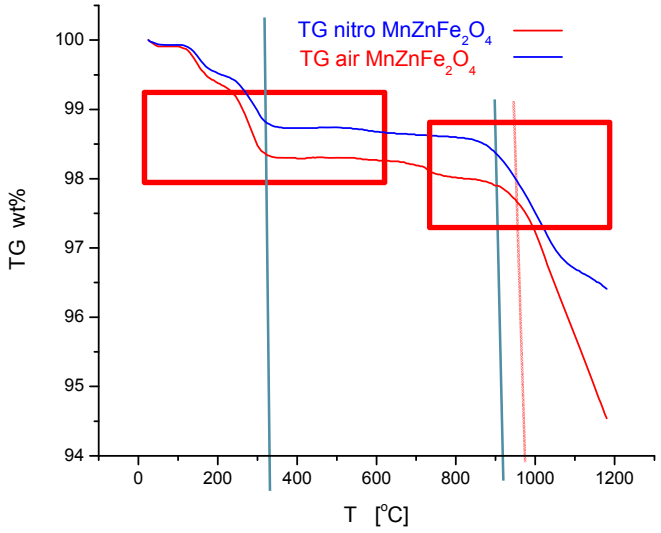


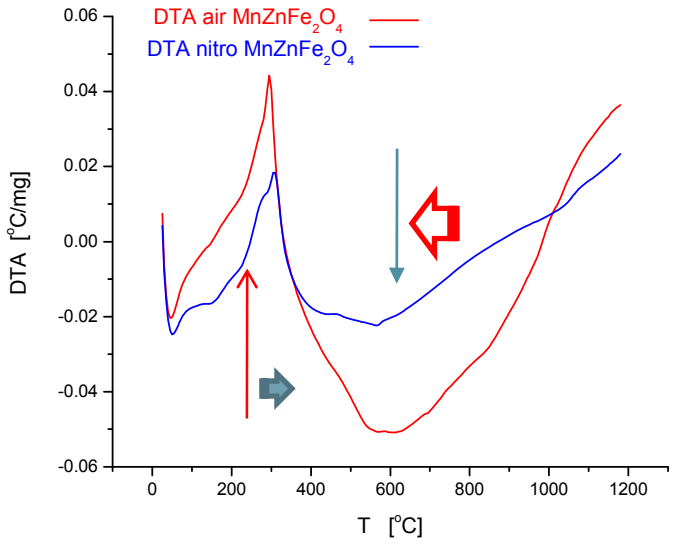


Dilatometry and TG/DTA
$Mn_{1-x}Zn_xFe_2O_4$



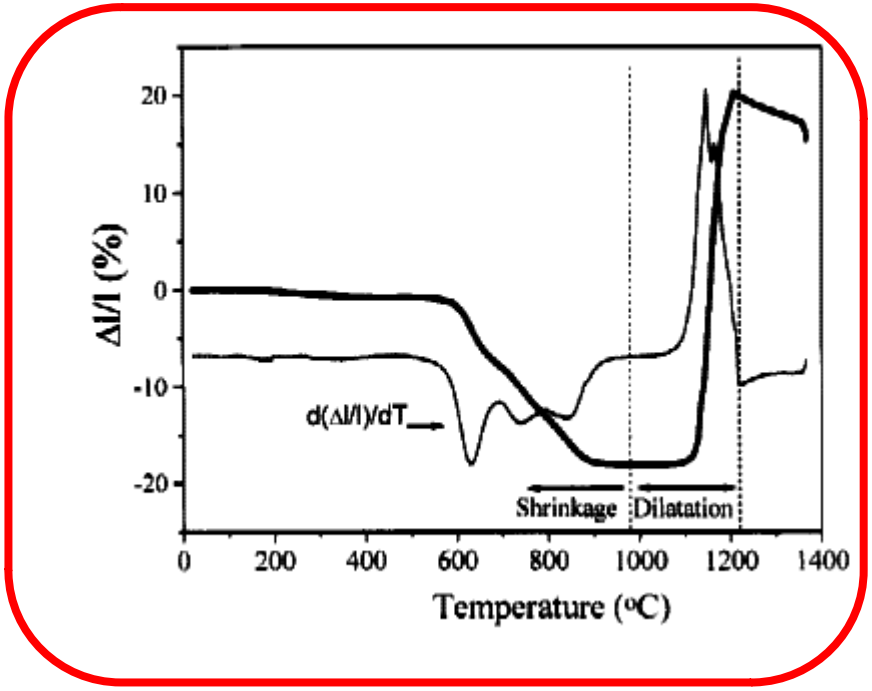




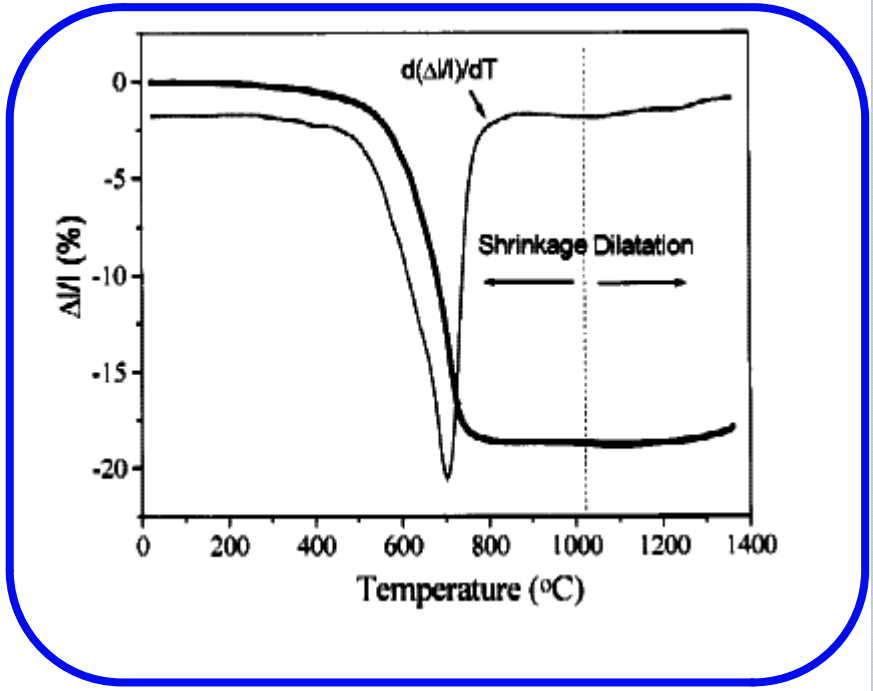


$$2Mn_{0.5}Zn_{0.5}Fe_2O_4 + \frac{1}{4}O_2 \underset{900°C}{\overset{700°C}{\rightleftharpoons}} Fe_2O_3 + \frac{1}{2}Mn_2O_3 + ZnFe_2O_4$$

Air



Nitrogen



J. Am. Ceram. Soc., 81 [7] 1757–64 (1998)

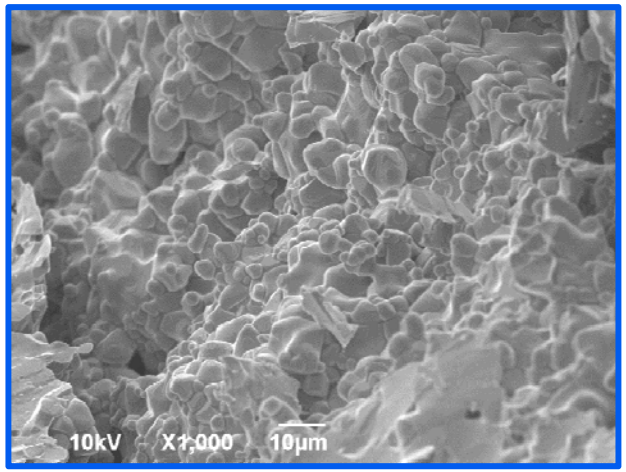
Sintering of Nanosized MnZn Ferrite Powders

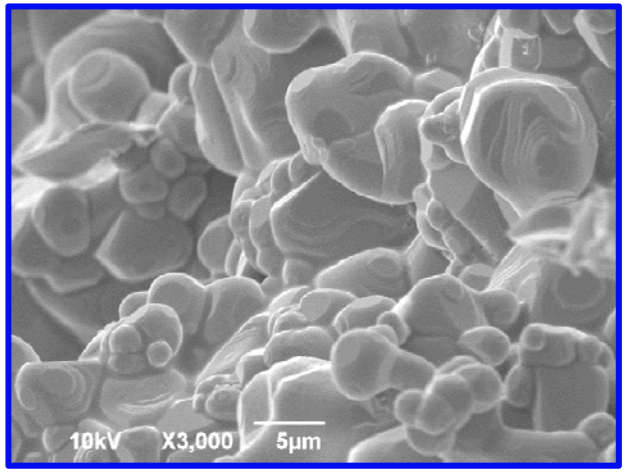
Marko Rozman and Miha Drofenik*

Jožef Stefan Institute, Ljubljana, Slovenia

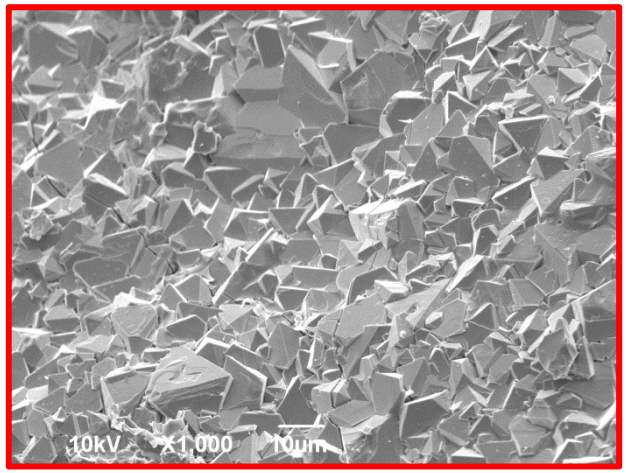
SEM $Mn_{1-x}Zn_xFe_2O_4$

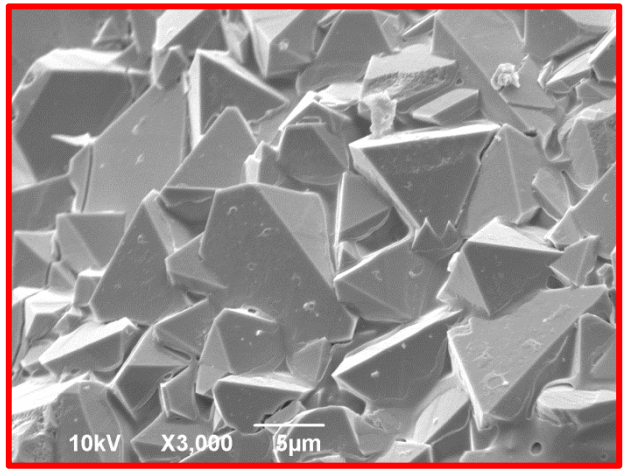
Nitrogen



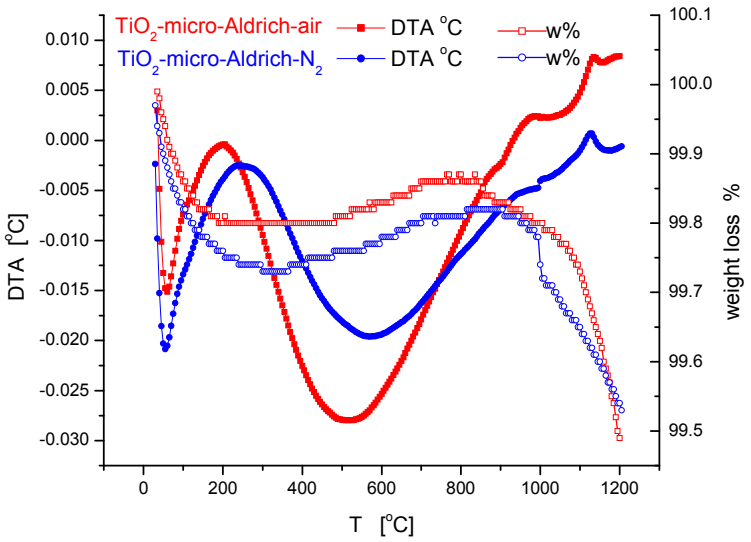


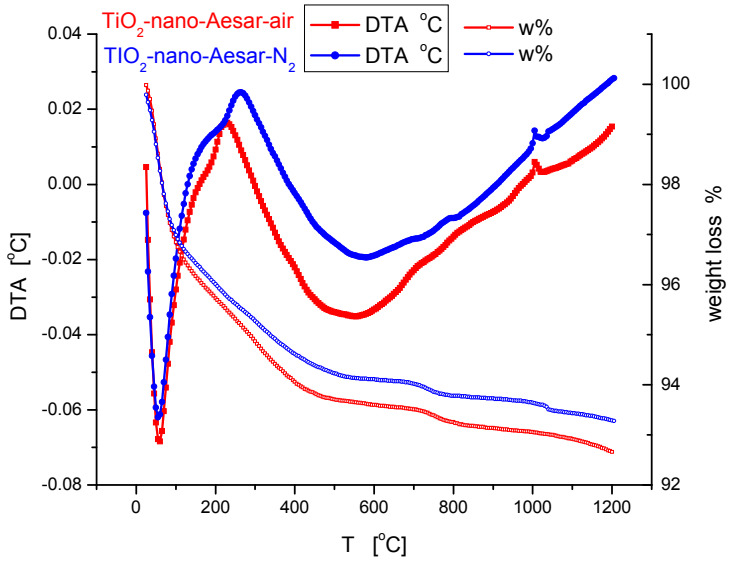
Air





TiO_2 nano powder
TiO_2 micro powder
TG/DTA





Science of Sintering, **46** (2014) 365-375

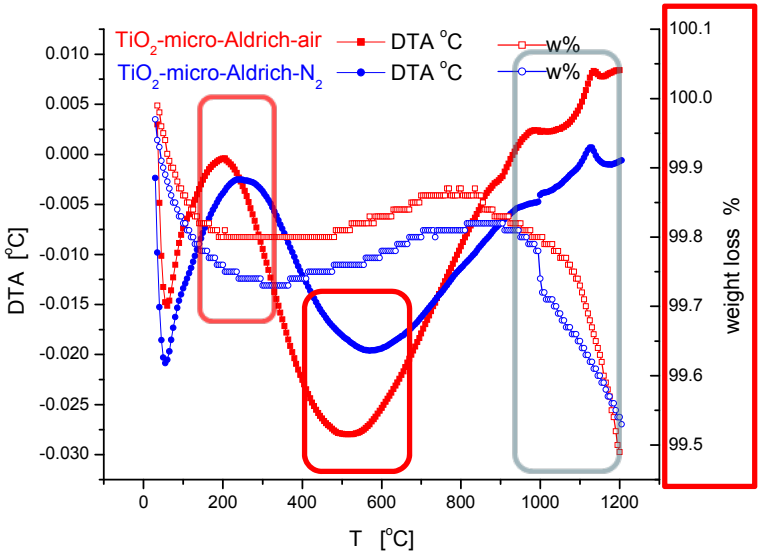
doi: 10.2298/SOS1403365L

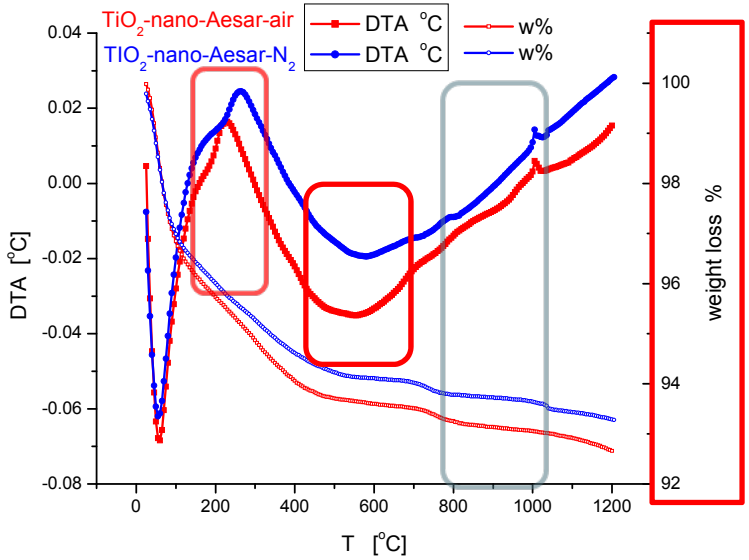
UDK 549.514; 622.785

Influence of Nitrogen and Air Atmosphere During Thermal Treatment on Micro and Nano Sized Powders and Sintered TiO_2 Specimens

N. Labus[1*], S. Mentus[2,3], Z. Z. Đurić[1], M. V. Nikolić[4]

TiO_2 nano powder
TiO_2 micro powder
TG/DTA





Science of Sintering, **46** (2014) 365-375

doi: 10.2298/SOS1403365L

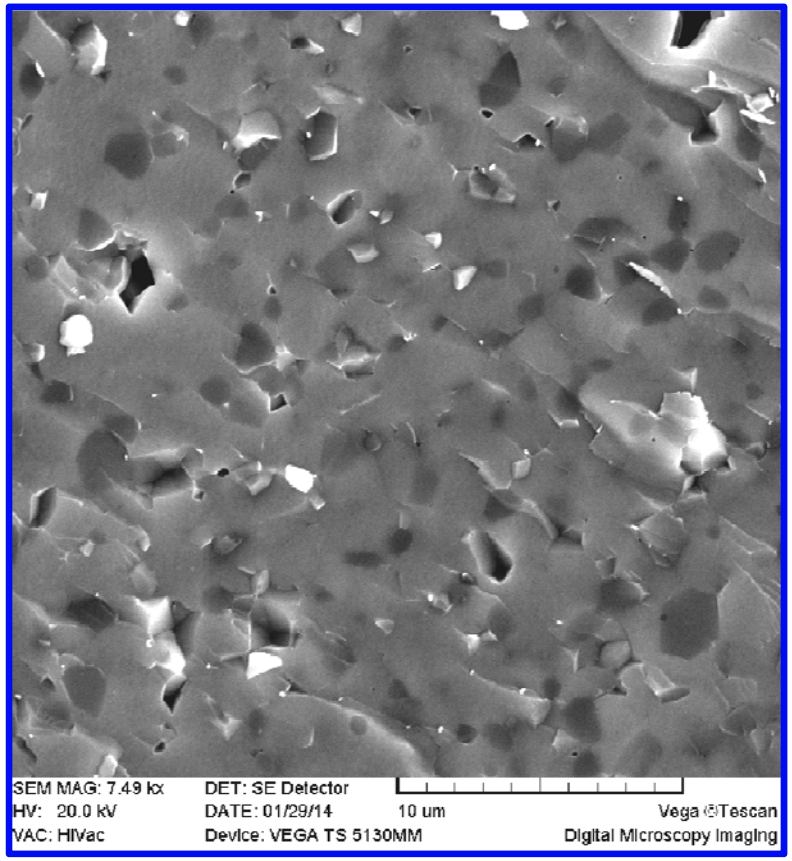
UDK 549.514; 622.785

Influence of Nitrogen and Air Atmosphere During Thermal Treatment on Micro and Nano Sized Powders and Sintered TiO_2 Specimens

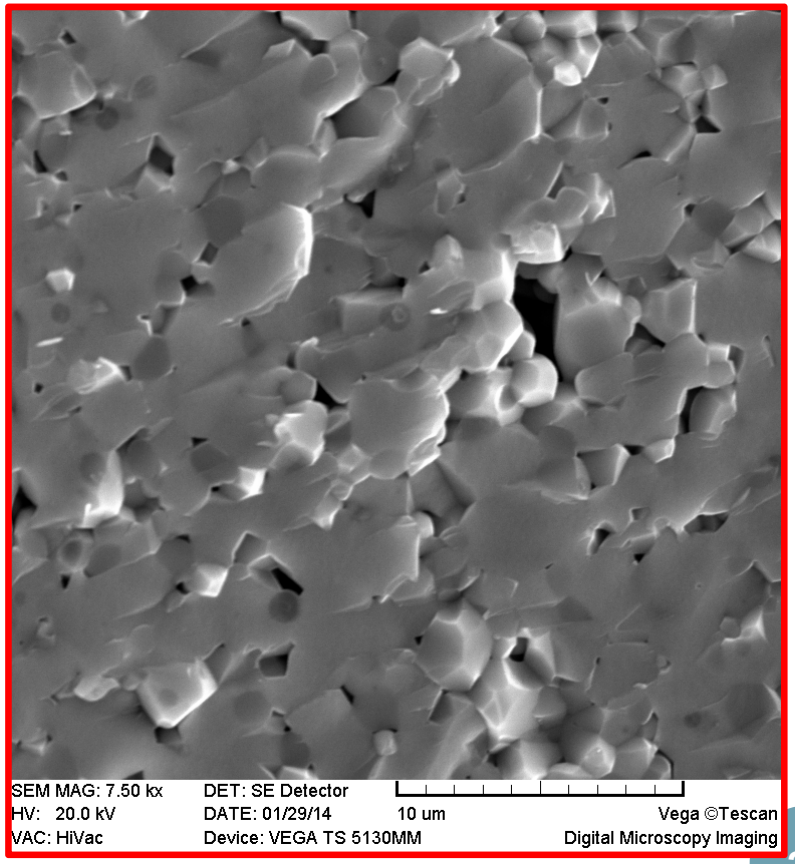
N. Labus[1*)], S. Mentus[2,3], Z. Z. Đurić[1], M. V. Nikolić[4]

SEM TiO_2 sintered - reheated

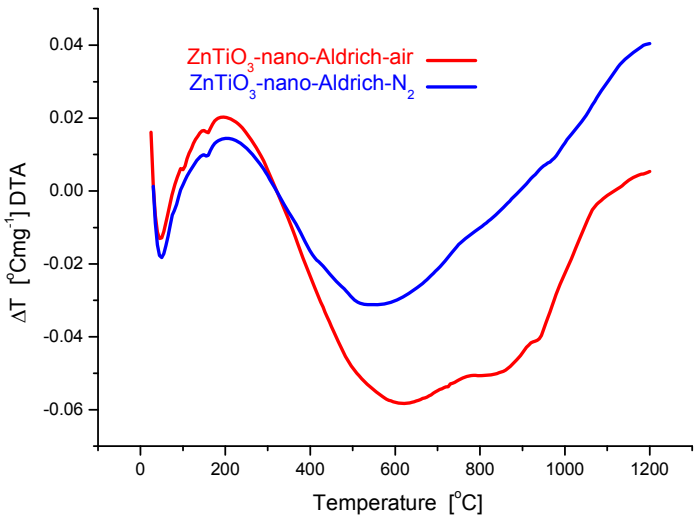
Nitrogen

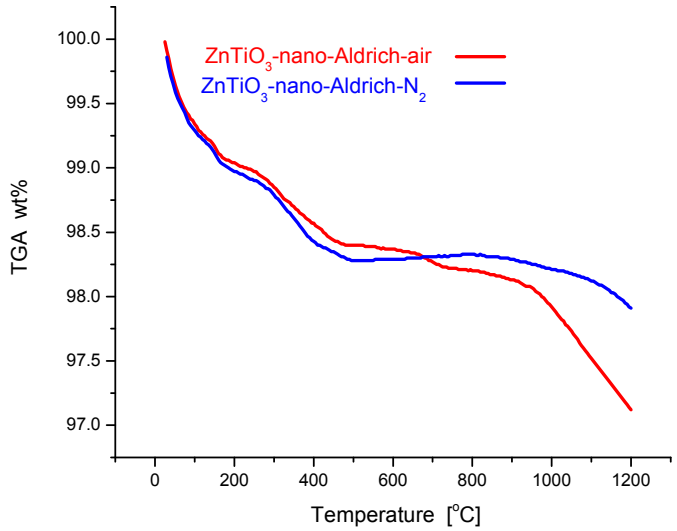


Air



$ZnTiO_3$ nano powder TG/DTA





Science of Sintering, **47** (2015) 71-81

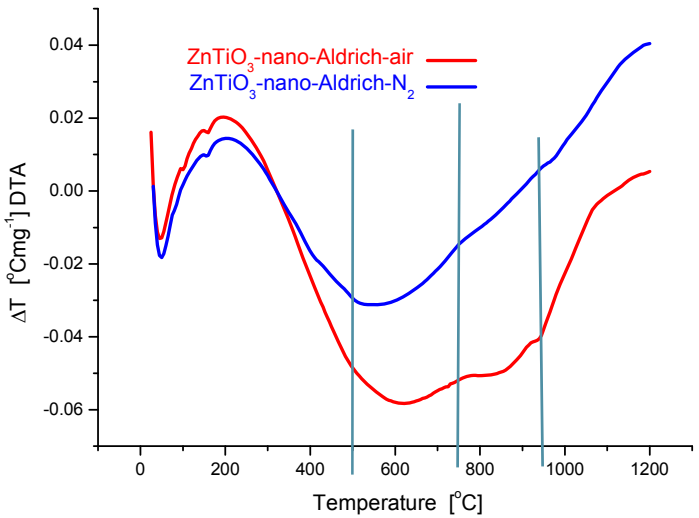
doi: 10.2298/SOS1501071L

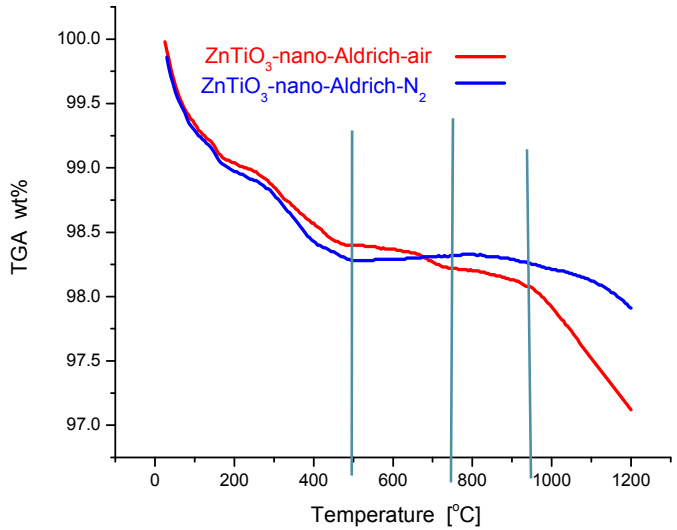
UDK 622.785; 546.824

Reheating of Zinc-titanate Sintered Specimens

N. Labus[1*)], S. Mentus[2,3], S. Rakić[4], Z. Z. Đurić[1], J. Vujančević[1], M.V. Nikolić[5]

$ZnTiO_3$ nano powder TG/DTA





Science of Sintering, **47** (2015) 71-81

doi: 10.2298/SOS1501071L

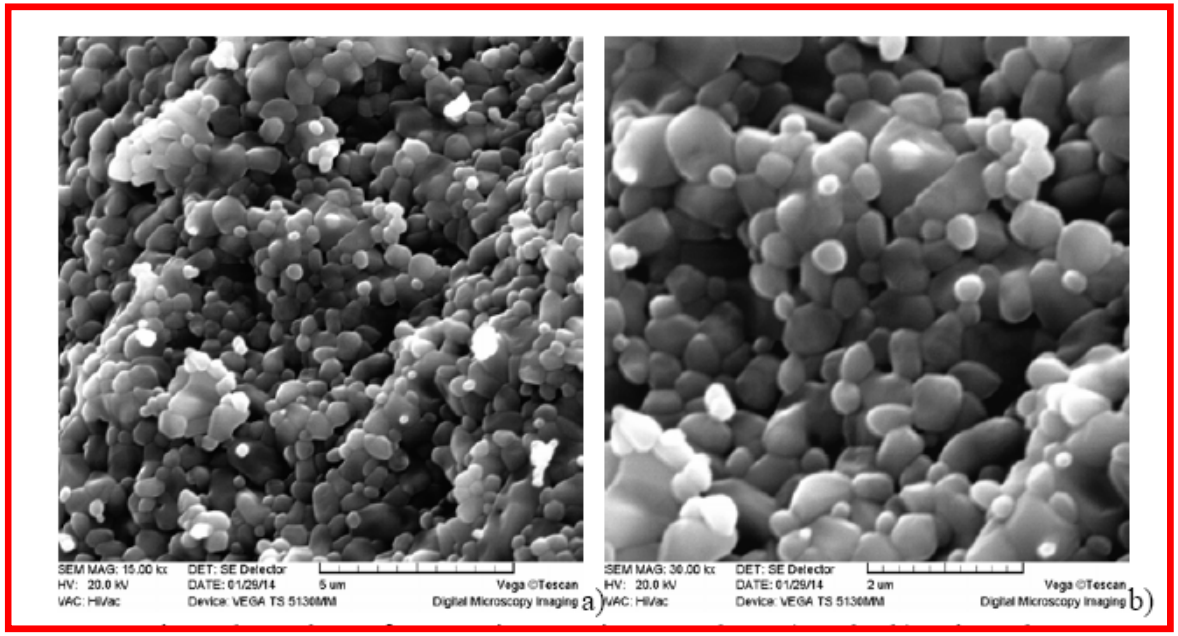
UDK 622.785; 546.824

Reheating of Zinc-titanate Sintered Specimens

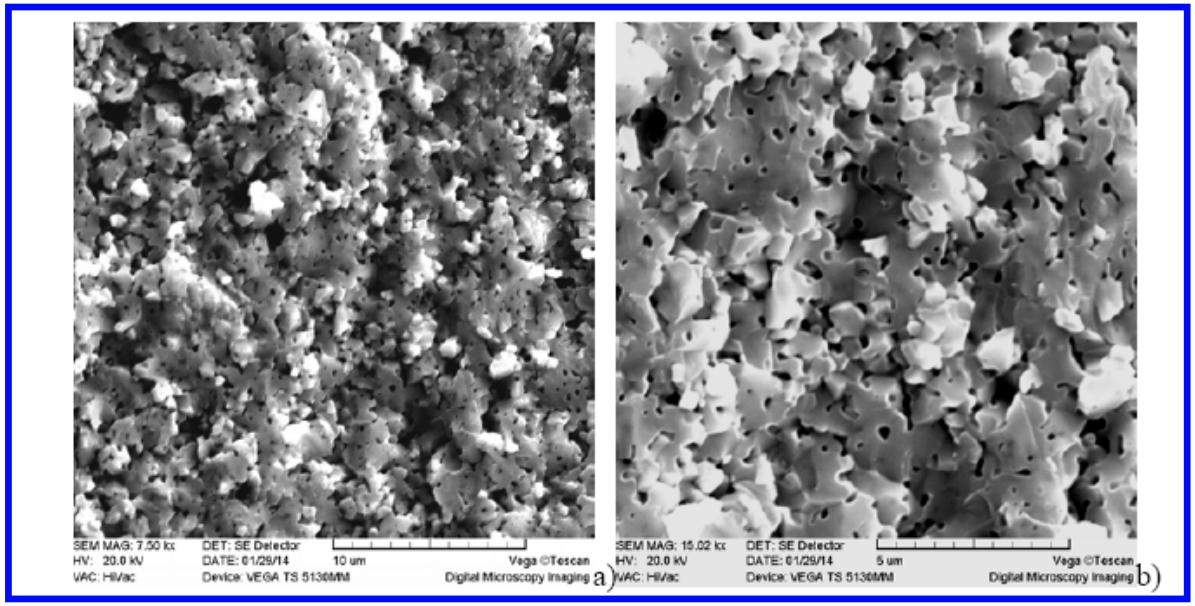
N. Labus[1*)], S. Mentus[2,3], S. Rakić[4], Z. Z. Đurić[1], J. Vujančević[1], M.V. Nikolić[5]

SEM $ZnTiO_3$ sintered - reheated

Air



Nitrogen



CONCLUSION

- Oxides TiO_2, $ZnTiO_3$ and $Mn_{1-x}Zn_xFe_2O_4$ showed different dimension changes behavior during heating in air and nitrogen atmosphere.
- Microstructures observed on breakage showed completely different structure.
- Thermo gravimetric and differential thermal analysis showed that powder particle size plays fundamental role in atmosphere influence.