JEMS 20 18 Joint European Magnetic Symposia

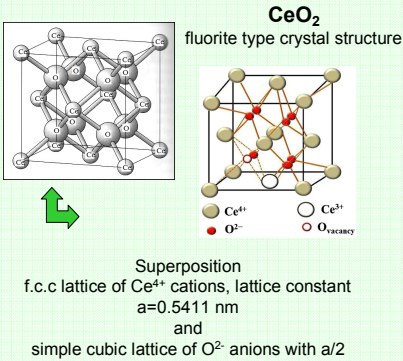# Effect of iron impurities on magnetic properties of nanosized CeO₂ and Ce-based compounds

UNIWERSYTET ŚLĄSKI W KATOWICACH

A. Chrobak
Institute of Physics, University of Silesia in Katowice
Uniwersytecka 4, 40-007 Katowice, Poland

UNIVERZITA J. E. PURKYNE V USTI NAD LABEM

P. Janos
Faculty of the Environment
Králova Výšina 7
400 96 Ústí nad Labem, Czech Republic

ipm
Y. Jirásková and J. Buršík
jirasko@ipm.cz
Institute of Physics of Materials
Academy of Sciences of the Czech Republic
Žižkova 22, CZ-616 62 Brno, Czech Republic

J. Lunacek and O. Zivotsky
Department of Physics
VSB-Technical University of Ostrava
17.listopadu 15, 708 33 Ostrava-Poruba, Czech Republic

AIM To characterize cerium oxide CeO₂, known as ceria, from structural and physical viewpoint and to solve puzzle concerning magnetic behaviour in its nanocrystalline form.

Ce – Cerium - basic properties
- chemical element, atomic number 58
- silver-white metal
- second element in the lanthanide series
- showing +3 and also +4 oxidation states
- the most widely used compound is CeO₂

CeO₂ – Ceria - basic properties
- fluorite crystal structure-f.c.c-unit cell - space group Fm3m
- pale yellow colour
- insoluble in water
- moderately soluble in strong mineral acids
- hygroscopic absorbing small amounts of moisture and CO₂ from the atmosphere
- diamagnetic in its bulk form
- easy formation of oxygen vacancies
- ferromagnetic (?) in nanocrystalline form

CeO₂ fluorite type crystal structure

○ Ce⁴⁺   ○ Ce³⁺   ● O²⁻   ○ O_vacancy

Superposition
f.c.c lattice of Ce⁴⁺ cations, lattice constant a=0.5411 nm
and
simple cubic lattice of O²⁻ anions with a/2

Sample preparation

Cerium oxide samples S4, S5, and S6 were prepared from the same cerium source - cerium (III) nitrate hexahydrate using different precipitation procedures:

S4 was prepared by conventional direct precipitation of the cerous nitrate solution with the saturated solution of oxalic acid.

S5 was prepared by homogeneous precipitation with dimethyl oxalate.

In both cases, the resulting cerous oxalates were dried and annealed at 500 °C for 2 hours in air atmosphere to convert them into cerium oxides.

S6 was prepared by a well-established precipitation/calcination synthetic route using ammonium carbonate as precipitant with subsequent calcination at 500 °C.

Chemicals used

cerium (III) nitrate hexahydrate, oxalic acid, dimethyl oxalate and ammonium bicarbonate were obtained from Sigma-Aldrich as reagent-grade chemicals with purity above 99%. All solutions were prepared in deionized water obtained from a Demi Ultra 20 system (Goro, Prague, Czech Republic) in which reverse osmosis and mixed-bed ion-exchange were used for water purification.

Morphology, chemical and phase composition

SEM TESCAN LYRA 3XMU FEG/SEM scanning electron microscope: accelerating voltage of 20 kV, equipped with an XMax80 Oxford Instruments detector for energy-dispersive X-ray analysis (EDX)

Mean chemical composition in at. %

EDX

		area		point	
S4	Ce	28.36	± 4.56	19.07	± 4.12
	O	71.64		80.93	
S5	Ce	28.55	± 0.21	30.75	± 13.94
	O	71.45		69.25	
S6	Ce	27.88	± 0.37	26.20	± 2.66
	O	72.12		73.80	

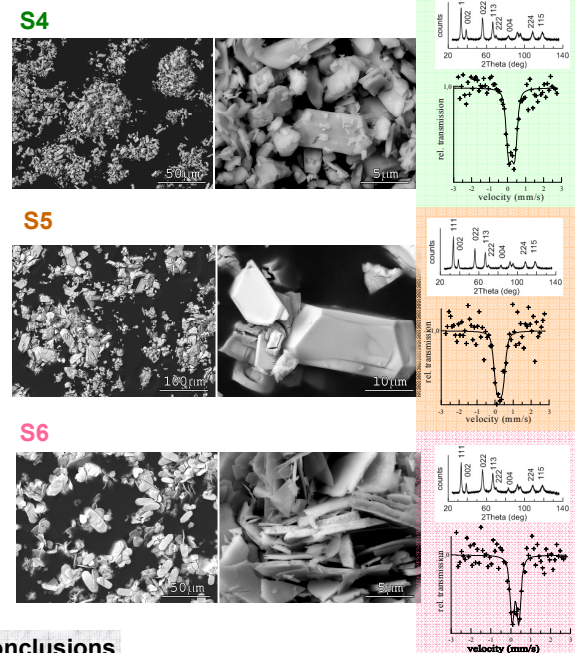**XRD** X'PERT PRO diffractometer (Panalytical); Co Kα radiation (λ = 0.17902 nm), 2θ = 20° - 135°, steps = 0.01°, time/step 5 s. Rietveld structure refinement method using the HighScore Plus program; ICSD database

ICSD 28753 for CeO₂	
a (nm)	d (nm)
S4 0.5414(1)	15.1
S5 0.5413(1)	21.8
S6 0.5415(1)	19.0

S4

S5

S6

An origin of ferromagnetic behavior of CeO₂ nanoparticles is ascribed to:

- formation of localized electron spin moments at the oxygen vacancies in particular present at nano-particle surfaces,
- effects of Ce³⁺ ions on the nanoparticle surfaces which carry their own magnetic moments contrary to diamagnetic Ce⁴⁺ ions.
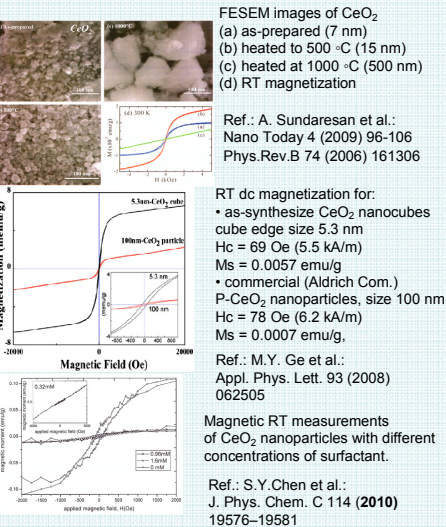
Are only these phenomenon sufficient to explain ferromagnetic behaviour of CeO₂ nanoparticles?

Selected results

FESEM images of CeO₂
(a) as-prepared (7 nm)
(b) heated to 500 °C (15 nm)
(c) heated at 1000 °C (500 nm)
(d) RT magnetization
Ref.: A. Sundaresan et al.: Nano Today 4 (2009) 96-106 Phys.Rev.B 74 (2006) 161306

RT dc magnetization for:
- as-synthesize CeO₂ nanocubes cube edge size 5.3 nm Hc = 69 Oe (5.5 kA/m) Ms = 0.0057 emu/g
- commercial (Aldrich Com.) P-CeO₂ nanoparticles, size 100 nm Hc = 78 Oe (6.2 kA/m) Ms = 0.0007 emu/g,
Ref.: M.Y. Ge et al.: Appl. Phys. Lett. 93 (2008) 062505

Magnetic RT measurements of CeO₂ nanoparticles with different concentrations of surfactant.
Ref.: S.Y.Chen et al.: J. Phys. Chem. C 114 (2010) 19576–19581

Magnetic properties

Quantum Design XL-7 superconducting quantum interference device (SQUID) magnetometer.

300 K and 2 K hysteresis loops consist of dia-, para-, and ferromagnetic contributions

Diamagnetic: ● reflected by decrease of magnetization at higher mag. fields, ● described by a negative magnetic susceptibility χ_D, ● practically independent on the applied temperature.

Paramagnetic: ● well determined from the 2 K magnetic measurements, ● dependent on temperature following Curie-Weiss law

Ferromagnetic: ● reflected by sharp magnetization (300 K) reversal at lower field, ● originated in a large number of structural defects (surface oxygen vacancies) and/or magnetic impurities, ● small magnetization of order of 10⁻³ Am²/kg

	χ_D (m³/kg)	Msfm 300K (Am²/kg)	Conc.Fe (ppm)	Mspm 2K (Am²/kg)	Conc. Ce³⁺ (-)
S4	-4.49*10⁻⁹	0.002	9	0.028	0.0009
S5	-1.11*10⁻⁸	0.0008	3	0.045	0.0015
S6	-2.10*10⁻⁸	0.0014	6	0.160	0.0052

S4   300 K   2 K

---- Brillouin function

after correction

S5

S6
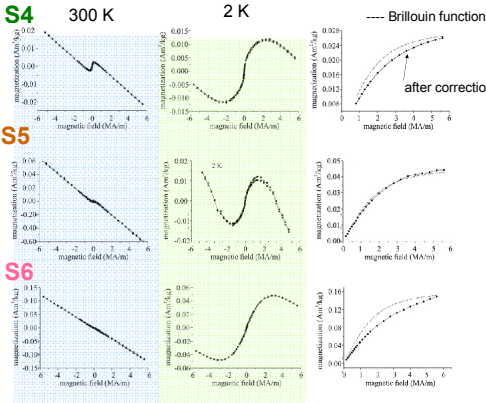
Conclusions

- The room and low temperature magnetic measurements of the samples prepared by two different procedures from different chemicals clearly evidence the diamagnetic, paramagnetic, and ferromagnetic contributions to their magnetic behaviour.
- The effect of Ce³⁺ ions as carriers of own magnetic moment can be excluded due to their insignificant concentration compared to diamagnetic Ce⁴⁺ ions in ceria samples.
- Fe impurities detected by chemical analysis and confirmed by Mössbauer spectrometry play a significant role in nanosized ceria despite their small amount.
- Fe impurities detected in ppm amount in input chemicals are not fully removed by procedures used for ceria production.

well-established Fe in ceria impeaches the effect of oxygen vacancies as a unique source of ceria magnetism.

⁵⁷Fe Mössbauer spectrometry

was used to confirm or to exclude prospective contamination of the samples and selected chemicals with iron impurities.

- RT measurements in standard transmission geometry, 57Co(Rh) source
- calibration of the velocity scale - Mössbauer spectrum of α-Fe => determining isomer shifts
- all spectra evaluated using the transmission integral approach in the program CONFIT
- experimental points analysed by double- and/or single-line components yielding values of isomer shift (δ) and quadrupole splitting (Δ).

Samples

	δ (mm/s)	Δ (mm/s)
S4	0.229(10)	0.316(15)
S5	0.251(19)	0.303(34)
S6	0.232(12)	0.333(18)

Chemicals

	δ (mm/s) / Δ (mm/s)
cerous chloride 3N-C (99.9%, 2.83 ppm Fe)	0.218(68) / -
cerium nitrate 5N-N (99.999, 3.61 ppm Fe)	0.397(43) / 0.118(106)
cerous carbonate (p.a.)	0.374(31) / -

ICP-AES