

Supplementary Material (ESI) for Journal of Materials Chemistry
This journal is © The Royal Society of Chemistry 2007

Electronic supplementary information

Large-scale preparation of ceria/bismuth metal-matrix nano-composites with a hardness comparable to steel

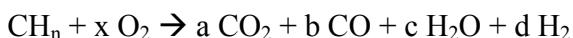
Robert N. Grass¹, Thomas F. Albrecht¹, Frank Krumeich² and Wendelin J. Stark^{1,*}

Flame temperature and residence time

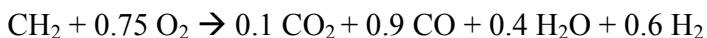
The adiabatic flame temperature can be calculated from the enthalpy of reaction and the heat capacity of the flame off gas:

$$\Delta T = \frac{\Delta_r H}{\sum_{x=1}^i c_{p,x} n_x}$$

where ΔT is the temperature rise, $\Delta_r H$ is the enthalpy of reaction, $c_{p,x}$ is the molar heat capacity of product x and n_x is the amount of component x in the flame off-gas. To be able to calculate the enthalpy of reaction for a sub-stoichiometric combustion reaction:



the coefficients a,b,c and d have to be measured. Here this has been done by measuring the gas composition in the flame off-gas using a mass spectrometer resulting in the following coefficients which are in agreement with prior thermodynamic calculations (Grass, R. N.; Stark, W. J. *J. Mater. Chem.* **2006**, 16, 1825.):



Whereas the enthalpy of reaction and the heat capacities can be found from reference data (*CRC Handbook of Chemistry and Physics*, 78^{edn.}; CRC Press.: New York, 1997.) the composition of the off-gas stream (n_x) was evaluated from the mass-spectroscopy data adding the nitrogen stream feed to the flame through the porous tube. Assuming full radial mixing and the completion of the combustion reaction half way up the tube the adiabatic flame temperature can be calculated to be 1040°C, quickly cooling to 700°C at the end of the tube. This is well in agreement with measurements using a thermocouple in the flame off-gas preformed at 1 cm above the porous tube where the flame has cooled to 610°C.

The residence time of the particles in the tube can be calculated assuming an average temperature in the tube of 800°C as < 100 ms.

It has to be said, however, that the exact temperature present in the flame as well as the residence time is very hard to predict, as turbulent flames are only poorly understood (e.g. Jenny, P.; Pope, S. B.; Muradoglu, M.; Caughey, D. A. *J. Comput. Phys.* **2001**, 166, 218.) and the measurement of temperatures in flames is complex (e.g. Arabi-Katbi, O. I.; Pratsinis, S. E.; Morrison, P. W.; Megaridis, C. M. *Comb. Flame* **2001**, 124, 560.) often needing correction factors due to radiation losses (e.g. Francis, J.; Yau, T. M. *Fire Technol.* **2004**, 40, 277.).

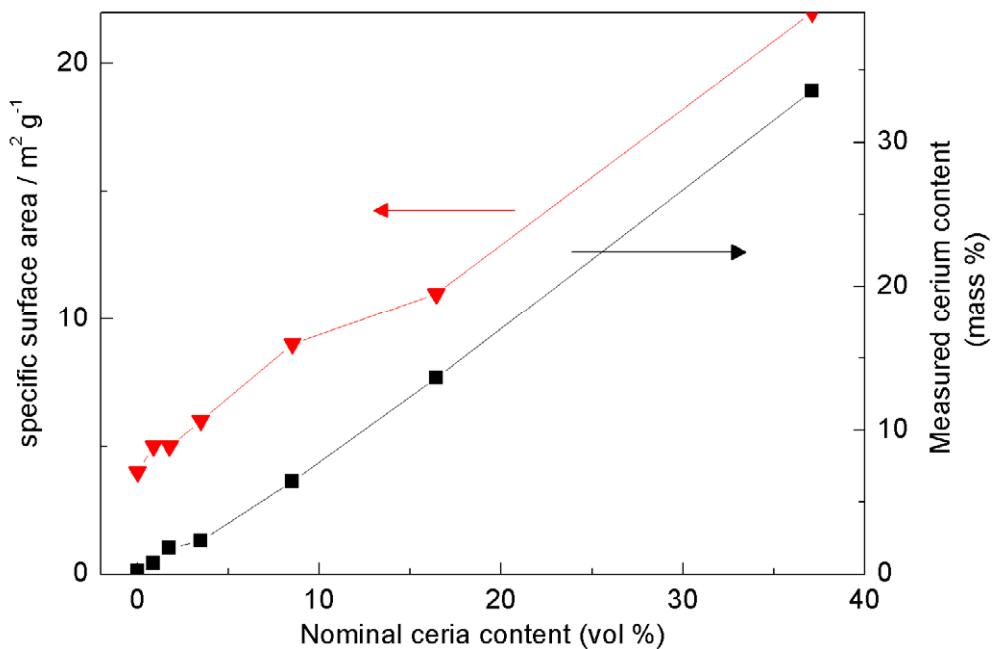


Figure S1. Particle specific surface area (red triangles) measured by nitrogen adsorption²⁹ and cerium content (black squares) measured by electron dispersive X-Ray analysis as a function of the nominal ceria content.

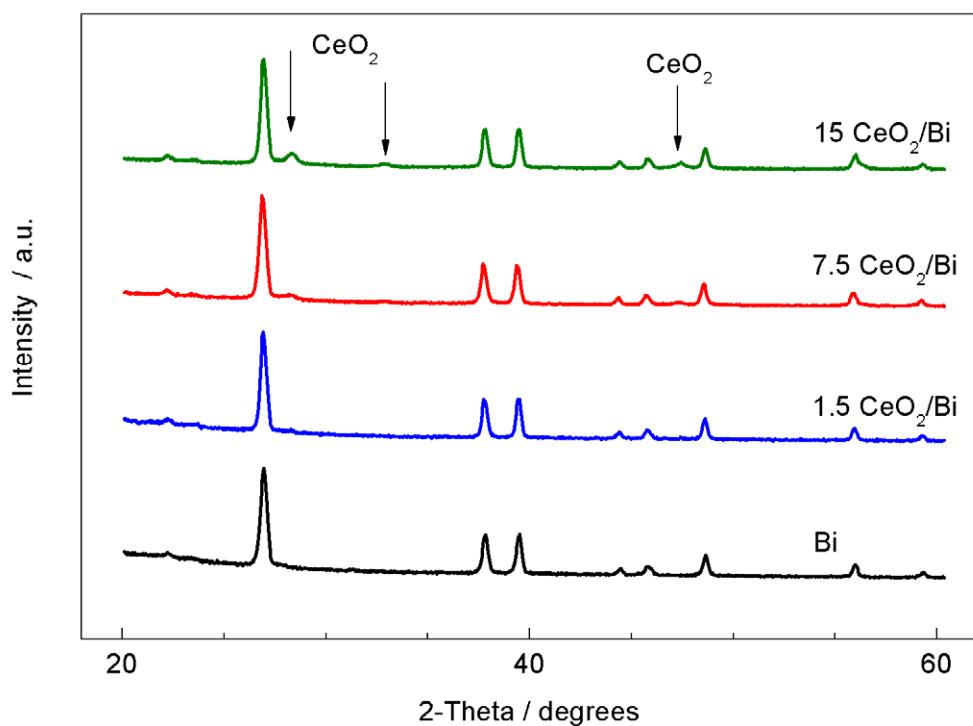


Figure S2. X-ray diffractograms of the produced powders at various ceria/bismuth volume fractions. The lowest line represents pure as-prepared metallic bismuth nanopowder. As the cerium concentration of the precursor increases ceria peaks can be observed in the diffractograms (top line). The ceria content is given in nominal vol%. The apparent absence of cerium oxide peaks in the 1.5 CeO₂/Bi sample (3rd line from top) can be accredited to the detection limit of X-ray diffraction.

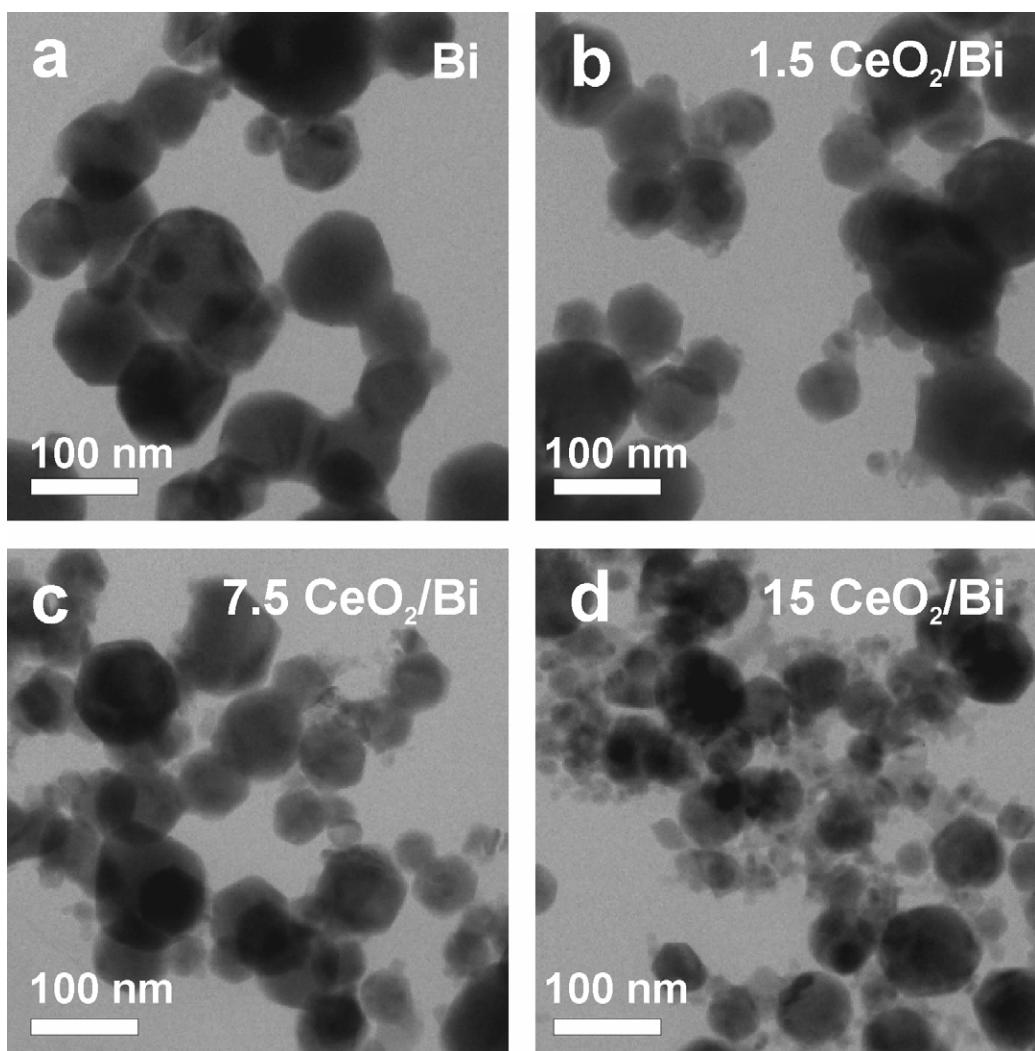


Figure S3. Transmission electron micrographs of as-prepared bismuth nanopowder (a) showing nearly spherical particles of diameters between 20 and 100 nm. Increasing the cerium content in the precursor resulted in the additional formation of smaller cerium-oxide clusters.

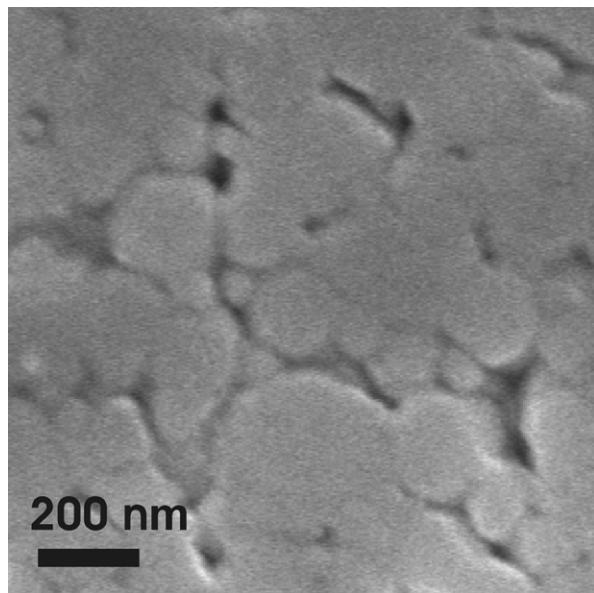


Figure S4. Surface of a pill pressed from pure bismuth nano-powder depicting a grain-size slightly above the particle size of the as-prepared nano-powder and some residual porosity.

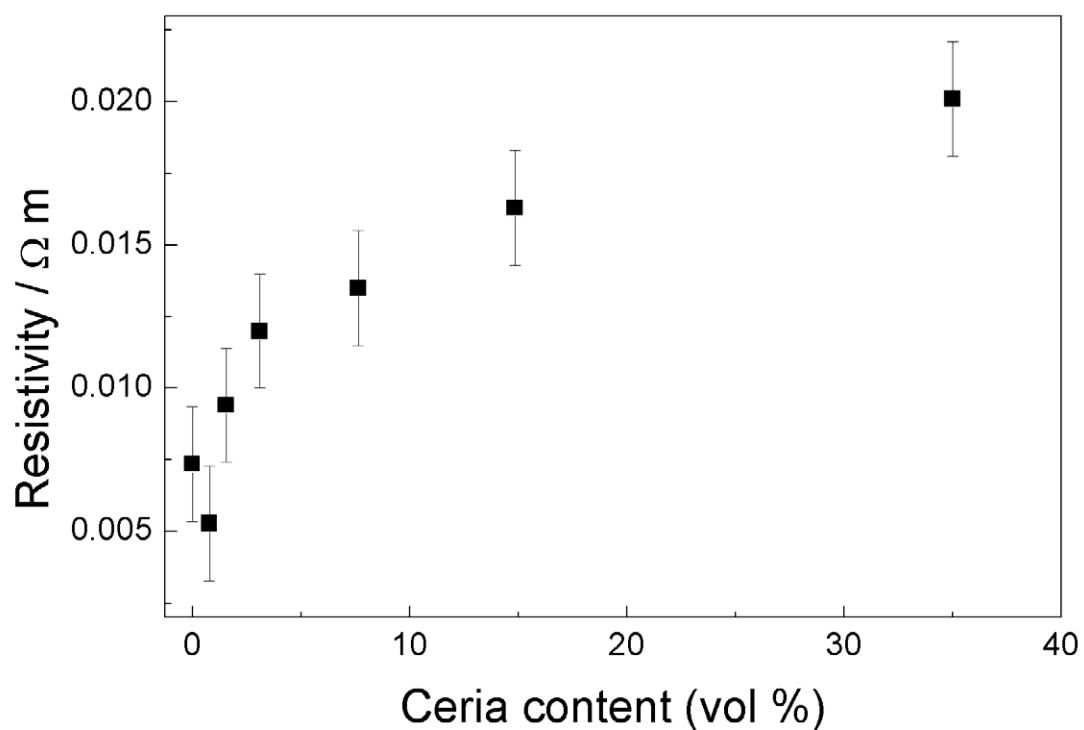


Figure S5. Pill electrical resistivity as a function of the ceria content measured by the two-point method in air (Voltcraft, VC 200, error bars are calculated from measurement error).