



Structure and magnetic properties of synthesized fine cerium dioxide nanoparticles

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ABSTRACT

Cerium dioxide, which is diamagnetic in its bulk crystalline fluorite form, exhibits ferromagnetism when prepared as a nanopowder. This characteristic has recently been ascribed to localized electron spin moments formed at oxygen vacancies near the nanoparticle surfaces. In the present study, a number of structure-sensitive and magnetic methods were applied to CeO₂ nanopowders prepared from the carbonate precursor by treatment at different calcination temperatures. The low-temperature magnetization measurements subsequently performed via ⁵⁷Fe Mössbauer spectroscopy revealed the presence of small amounts of iron impurities in the samples as well as in the chemicals used to prepare them. These experimental findings and our theoretical data analysis of iron impurities at the ppm level provide a plausible explanation for the ferromagnetic behaviour of cerium oxide.

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1. Introduction

Cerium is a rare-earth element that can exist either as a free metal or in one of two oxide forms: cerous (cerium(III)) or ceric (cerium(IV)). Fig. 1 shows cerium dioxide, CeO₂, in a fluorite-like structure in which each Ce site is surrounded by 8 O sites in a face-centred-cubic (fcc) arrangement and each O site has 4 neighbouring Ce sites. Typically, some Ce³⁺ ions are present in the structure of cerium (di)oxide; the number of these ions is related to the number of oxygen vacancies [1].

Cerium oxide is used in diverse industries as a glass-polishing agent [2], in protective coatings of metal alloys [3], in solar cells [4] and in gas sensors [5]. It plays a prominent role in heterogeneous catalysis (as a part of automobile exhaust systems [6]), and numerous studies have been devoted to its photocatalytic applications in environmental protection [7–9]. Recent studies have shown that some forms of cerium oxide can catalyse biologically

relevant reactions in a manner similar to conventional enzymes. Hence, nanoparticulate cerium oxide (nanocerium) has been classified as a “nanozyme” and used, e.g., in the treatment of neurodegenerative diseases, for which its redox properties are exploited [10,11]. In addition, the phosphatase-mimetic ability of cerium oxide (its ability to break phosphoester bonds [12–14]) has been utilized to degrade dangerous organophosphate compounds, including some pesticides and chemical warfare agents [15,16].

Nanocrystalline metal oxides exhibit some unusual features not found in their bulk counterparts [17,18]. Most of these features are related to the dramatic changes in surface-to-volume ratio that occur when particle size is decreased to the nanometre level. Size-induced lattice expansions and relaxations [19,20], together with surface non-stoichiometry [21,22], generate active sites on the surface of cerium oxide, and these sites are responsible for its catalytic and enzyme-mimetic activities.

Nanocrystalline cerium oxide also exhibits some purely physical phenomena that have attracted the attention of scientists, such as ferromagnetic behaviour [23,24], which has promising applications in spintronics [25,26]. The magnetic behaviour of transition-metal-based oxides (iron oxides, CrO₂) originates from collective

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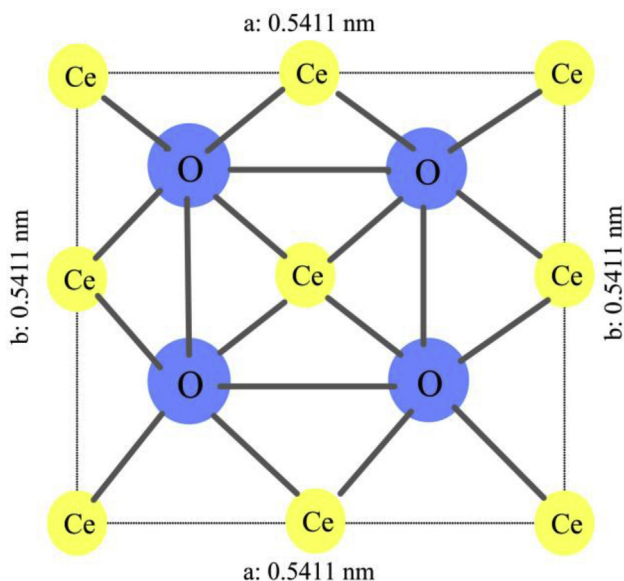


Fig. 1. Cubic structure of cerium dioxide, CeO_2 , with labelling of atoms.

interactions of the magnetic moments of atoms or ions that constitute the material. The atoms or ions are arranged in a periodic crystalline lattice, and their moments interact through a molecular exchange field, resulting in long-range magnetic ordering. However, CeO_2 , in which cerium exists as Ce^{4+} ($4f^0$ configuration), is a band insulator; its behaviour approaches diamagnetism. The hysteresis loop and the coercive field of approximately 8 kA/m with clear hysteresis dependence measured at 390 K in samples of Al_2O_3 nanoparticles smaller than 15 nm are surprisingly close to magnetic behaviour [23]. The origin of ferromagnetism in both of the aforementioned oxides has been ascribed to the presence of a large number of structural defects (oxygen vacancies) on the surfaces of the nanoparticles [24]. Although one can generalize that the magnetism is related to defects in the structure of the nanocrystals, its exact mechanism remains the subject of discussion; in particular, the role of dopants or impurities remains unclear [25,26]. As mentioned by Coey et al. [27], progress in this field is hampered by poor reproducibility of the published data, among other issues; this poor reproducibility may be related to the use of different cerium sources (their purity) and different procedures for cerium oxide preparation.

Nanoparticulate cerium oxides can be prepared using various technologies that can be roughly divided into two categories. In the low-temperature synthetic routes, cerium oxide is created by 'spontaneous' conversion from cerium hydroxide in an aqueous medium at relatively low temperatures ($<100^\circ\text{C}$). Dissolved oxygen serves as an oxidizing agent. The principle underlying this procedure is more than a century old [28]; nonetheless, it is still frequently used, especially for the preparation of enzymatically active nanoceria [29]. Modified versions of this procedure conducted in closed systems at elevated temperatures are suitable for the preparation of lanthanide-doped cerium oxides [8]. Industrial applications, however, usually require cerium oxides treated at temperatures $>500^\circ\text{C}$; such cerium oxides are typically prepared by thermal decomposition of suitable precursors (oxalates, carbonates) [2,16].

In the present work, a well-established precipitation/calcination procedure was used to prepare nanocrystalline cerium oxide. A relatively broad spectrum of experimental methods, some of which were applied at low temperatures, was used to examine the

changes in morphology, chemical composition and physical properties induced by calcination at various temperatures between 500 and 800°C . Detailed analysis of the obtained data should contribute to an understanding of the ferromagnetic behaviour of nanometre-sized cerium oxides.

2. Experimental

2.1. Materials and syntheses

A well-established precipitation/calcination synthetic route was used to prepare the cerium oxide samples [15,16]. Cerium(III) nitrate hexahydrate (p.a., $>99\%$, Sigma-Aldrich) and ammonium bicarbonate (p.a., $>99\%$, Sigma-Aldrich) were used as a cerium source and as a precipitant, respectively, in the cerium oxide synthesis. 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. In a typical experimental arrangement, 500 ml of an aqueous solution of cerium nitrate (0.2 mol/l) was mixed with an excess of ammonium bicarbonate (0.5 mol/l) to obtain insoluble cerium carbonate; reaction with oxalic acid was used to check the completeness of the precipitation. The reaction mixture was agitated using a magnetic stirrer for one hour and was then left undisturbed overnight. The finely crystalline precipitate of cerium carbonate was separated by filtration, thoroughly washed with deionized water, dried at 110°C and stored in a closed PE vessel; this material is hereinafter called precursor *E*. Cerium oxides were prepared by annealing precursor *E* for 2 h at pre-determined calcination temperatures of 500, 600, 700, and 800°C in an open porcelain crucible in a muffle furnace. All the sample preparation steps were performed with extreme care to avoid iron contamination. The samples are denoted *ET*, where *T* is the calcination temperature.

2.2. Structure characterization

Infrared (IR) spectra in the region $4000\text{--}400\text{ cm}^{-1}$ were recorded on a Nicolet Impact 400D spectrometer equipped with accessories for diffuse reflectance measurements. Raman spectra were acquired on a DXR Raman microscope (Thermo Scientific). Thirty-two two-second scans were accumulated with a laser (532 nm, 6 mW) under the $10\times$ objective of an Olympus microscope.

A Coulter SA3100 apparatus (Beckman, Krefeld, Germany) was used to determine the surface area of the particles and the porosity of the samples on the basis of physisorption via nitrogen adsorption/desorption. The Brunauer-Emmett-Teller and Barrett-Joyner-Halenda methods were used to calculate the surface area and to determine the pore size distribution, respectively.

X-ray diffraction patterns were measured at room temperature (RT) using an X'PERT PRO diffractometer equipped with a $\text{Co K}\alpha$ radiation source ($\lambda = 0.17902\text{ nm}$); the E500 sample was also measured at 4 K using a $\text{Cu K}\alpha$ radiation source ($\lambda = 0.1540598\text{ nm}$). All measurements were performed in the 2θ range from 25° to 135° in steps of 0.008° at a time per step of 3.5 s. The resultant powder patterns were evaluated by the Rietveld structure refinement method [30] in semiautomatic mode using the HighScore Plus program (Panalytical) and the ICSD database of inorganic and related structures [31]. In addition to the phase composition, the lattice parameters and the mean crystallite size, representing the size of coherently diffracting domains, were obtained from the pattern analysis.

A TESCAN LYRA 3XMU FEG/SEM scanning electron microscope operated at an accelerating voltage of 20 kV and equipped with an XMax80 Oxford Instruments detector for energy-dispersive X-ray

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