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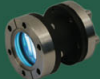



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Valence state dependent room-temperature ferromagnetism in Fe-doped ceria nanocrystals

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Room-temperature ferromagnetism was observed in undoped and Fe²⁺⁽³⁺⁾-doped CeO₂ nanocrystals. In Fe-doped samples the enhancement of ferromagnetic ordering occurs by changing the valence state of Fe ions, whereas Raman spectra demonstrated strong electron-molecular vibrational coupling and increase in oxygen vacancy concentration. Air annealing showed degradation of ferromagnetic ordering and appearance of hematite phase in Fe³⁺-doped sample. The observed ferromagnetic coupling in Fe-doped samples, associated with the presence of magnetic ions mediated by single charged O²⁻ vacancies, demonstrated that valence state of dopant has a strong influence on magnetic properties of CeO₂ nanoparticles. © 2010 American Institute of Physics.

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Ferromagnetic semiconductors with Curie temperature $T_c > 300$ K, are expected to play a vital role in the development of spintronics. The work of Matsumoto *et al.*¹ about the occurrence of ferromagnetism (FM) in Co-doped TiO₂ films initiated a lot of reports on FM above room temperature in different semiconductor oxide and nitride materials.²⁻⁶ Highly surprising was the discovery of room-temperature FM (RTFM) in semiconducting and insulating oxide thin films and nanopowders⁷⁻⁹ whose bulk counterparts are diamagnetic. The researchers in this field became aware of the phenomena, so called d^0 magnetism in nonmagnetic oxides, where defects and/or oxygen vacancies can be responsible for the observed FM. The question about importance of transition metal (TM) doping in introducing FM ordering in nonmagnetic oxide nanomaterials is still under controversy. Nevertheless, the semiconducting and/or insulating undoped and TM doped oxide nanomaterials became promising for spintronic application due to the reported FM at and above room temperature.^{3,4,9}

On the other side, it is firmly believed that the appearance of RTFM in cubic system will allow much easier integration of spintronic devices with advanced silicon based microelectronics. Among the materials with cubic symmetry, cerium oxide (CeO₂) presents an interesting candidate for advanced multifunctional devices because of variety of applications in catalysis, solid oxide fuel cells, optical coatings, etc. The recent discovery of RTFM in pure and/or doped CeO₂ nanopowders and thin films paves the road for the realization of future spintronic devices.¹⁰⁻¹²

In this work, we present the structural and magnetic properties of CeO₂ nanoparticles doped with 12% of different valence state Fe ions. The motivation for this work was to figure out the role and impact of oxygen vacancies and TM doping on the existing RTFM. We demonstrated that FM ordering through F center exchange mechanism is mediated by oxygen vacancies and strongly depends on the valence state of Fe dopant.

Nanocrystalline Ce_{1-x}Fe_x(Fe³⁺)O_{2-y} ($x=0$ and 0.12) powdered samples were prepared by the self-propagating room-temperature (SPRT) synthesis method.¹³ The structural characteristics of the samples were determined by x-ray powder diffraction (XRD) on a Siemens D-500 diffractometer with Cu K_α radiation. Room-temperature micro-Raman measurements were performed in backscattering configuration using a Jobin Yvon T64000 triple spectrometer with an Ar⁺/Kr⁺ laser of 514.5 nm. Room temperature Mössbauer spectra were obtained in standard transmission geometry with constant acceleration using a source of ⁵⁷Co in Rh (920 MBq). The magnetic properties of the samples were measured at room temperature using VSM 200-Cryogenic magnetometer.

Figure 1 shows the XRD patterns of Fe-doped CeO₂ nanopowders. All diffraction patterns show broad peaks, characteristic for small particles, which correspond to the CeO₂ with no traces of iron metal or oxide phases. The average particle sizes of pure and Fe²⁺⁽³⁺⁾-doped samples, calculated from Scherrer equation, were approximately 3 nm. In the inset of Fig. 1 is given AFM image of the

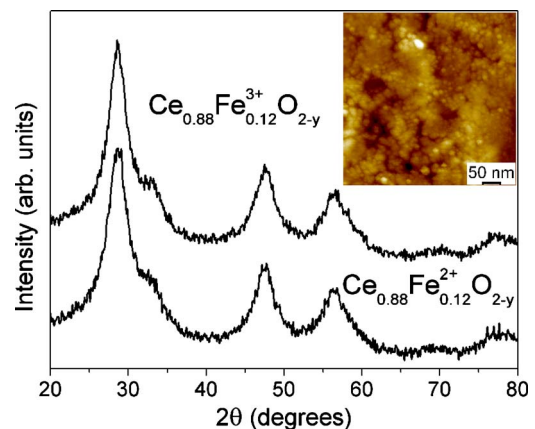


FIG. 1. (Color online) XRD spectra of Fe²⁺⁽³⁺⁾-doped ceria nanocrystalline samples. The inset shows AFM image of Fe³⁺-doped ceria sample.

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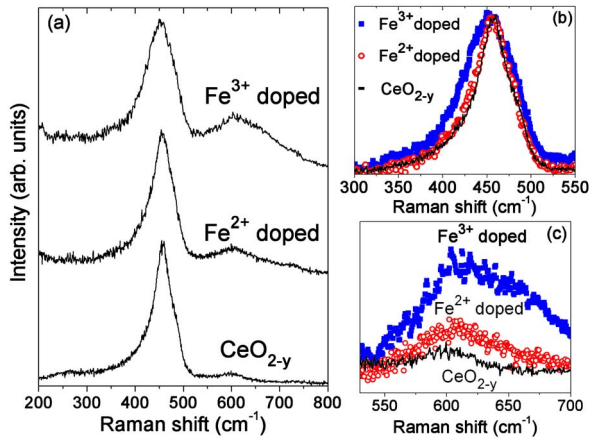


FIG. 2. (Color online) Raman spectra (a), behavior of F_{2g} mode (b), and intensity change in oxygen vacancy mode (c) of undoped and Fe-doped samples.

$Ce_{0.88}Fe_{0.12}^{3+}O_2$ sample which confirms that the sample is composed of very small nanoparticles.

In Fig. 2(a) room-temperature Raman spectra of pure and Fe-doped samples are presented. In the Raman spectra of all samples, F_{2g} mode characteristic for CeO_2 fluorite structure dominates. This mode in undoped sample is positioned at 454 cm^{-1} with pronounced asymmetry characteristic for very fine, nonstoichiometric nanocrystals.¹⁴ Another mode at 600 cm^{-1} originates from intrinsic oxygen vacancies.¹⁴ The Raman spectra confirmed XRD results that doped samples are solid solutions without presence of any Raman mode characteristic for iron-oxide phases.¹⁵ The additional redshift and broadening of the F_{2g} Raman mode [Fig. 2(b)] is noticed in the Fe^{3+} doped sample. Such behavior of the F_{2g} Raman mode was unexpected. The doping of ceria with $Fe^{2+(3+)}$ atoms of smaller ionic radius should cause the shrinkage of the unit cell and consequently shift in the F_{2g} mode to higher energies, i.e., blueshift. Raman spectra also demonstrated that $Fe^{2+(3+)}$ doping produces higher concentration of vacancies in ceria lattice [Fig. 2(c)] in order to ensure charge neutrality.

In Fe-doped samples, besides the existing $Ce^{3+}-V_0-Ce^{3+}$ complexes¹⁰⁻¹² (where V_0 denotes oxygen vacancy) the $Fe^{2+(3+)}-V_0-Fe^{2+(3+)}$ complexes are formed. Supposing that Fe^{2+} and Fe^{3+} ions are in a low spin state, Fe^{2+} -doping would produce only higher vacancy concentration whereas every Fe^{3+} ion which enters into ceria lattice brings additional charge. XRD results showed that undoped and doped samples have similar crystallite size (3 nm) imposing the conclusion that confinement effects cannot be responsible for the behavior of F_{2g} mode. Therefore, the observed and unexpected redshift and broadening of the F_{2g} mode in Fe^{3+} -doped sample can be only a consequence of strong electron molecular vibration coupling.¹⁶

RTFM was observed in both pure and Fe-doped samples (Fig. 3) after subtraction of linear paramagnetic component (lower inset of Fig. 3). The saturation magnetization (M_s) of undoped CeO_2 is about 5×10^{-3} emu/g. In Fe-doped samples, M_s increases with changing the valence state of dopant reaching the value almost four times higher ($\sim 2 \times 10^{-2}$ emu/g) for Fe^{3+} -doped sample.

The Mössbauer spectra of $Ce_{0.88}Fe_{0.12}^{2+(3+)}O_{2-y}$ samples (upper inset of Fig. 3), display paramagnetic doublet giving a

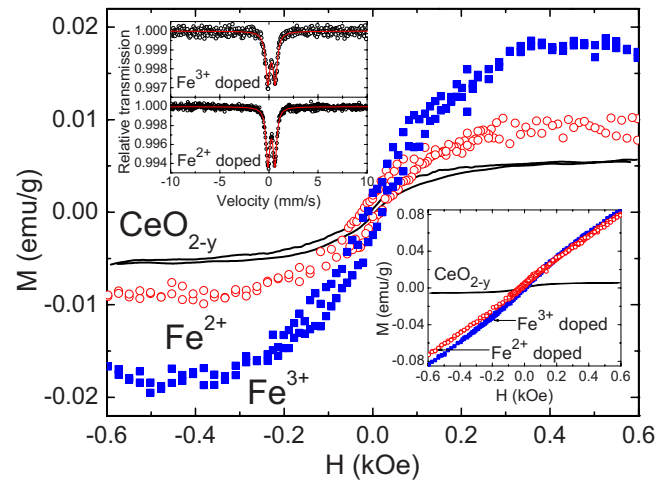


FIG. 3. (Color online) Room-temperature magnetization (M) vs field (H) for undoped and Fe-doped CeO_2 nanocrystals after subtracting the paramagnetic component. Lower inset shows raw experimental M - H data. Upper inset presents room temperature Mössbauer spectra of Fe-doped ceria samples.

strong indication that Fe ions exist in low spin state with a valence of 2+ (3+), respectively. The similar values of isomer shifts ($\delta=0.087\text{ mm/s}$ for Fe^{2+} and 0.090 mm/s for Fe^{3+} samples) relative to iron metal and quadrupole splitting ($\epsilon=0.721\text{ mm/s}$ for Fe^{2+} and 0.763 mm/s for Fe^{3+} samples) indicate that Fe^{2+} and Fe^{3+} ions entered substitutionally in ceria lattice but certain amount of Fe remained in the interstitial sites too. These isolated Fe ions are not magnetically ordered and contribute to paramagnetic behavior.

FM in CeO_2 nanocrystals is explained by several authors,^{9,10,12} as oxygen vacancy driven FM where each oxygen vacancy site, especially at the surface of nanoparticles, easily traps an electron from adsorption species¹² forming an F-center. The exchange interaction between the Ce^{3+} ions (with $4f^1$ configuration) and singly charged vacancy enables indirect FM coupling known as F-center exchange coupling (FCE).¹⁷

In Fe^{2+} doped sample, Fe^{2+} ions in the low spin ($3d^6$) state have no unpaired electrons and therefore $Fe^{2+}-V_0-Fe^{2+}$ complexes do not contribute much to the establishment of ferromagnetic ordering through FCE mechanism. Divalent iron produces only higher disorder in ceria lattice, i.e., slight increase in oxygen vacancies and $Ce^{3+}-V_0-Ce^{3+}$ complexes for charge neutrality. That is why the M_s value in Fe^{2+} -doped sample is little bit higher in comparison with undoped CeO_2 (see Fig. 3). On the contrary, in Fe^{3+} -doped sample, every Fe ion in low spin state ($3d^5$) has one unpaired electron spin which can participate in ferromagnetic ordering. Therefore, when Fe^{3+} ions enter substitutionally in ceria lattice besides an increase in vacancy concentration one can expect appearing of more ferromagnetic $Fe^{3+}-V_0-Fe^{3+}$ groups. The higher concentration of $Fe^{3+}-V_0-Fe^{3+}$ and $Ce^{3+}-V_0-Ce^{3+}$ complexes are responsible for FM coupling and significantly higher magnetization in this sample. Interpreting the complex magnetic behavior of Fe-doped CeO_2 we have to bear in mind that M_s value for Fe^{3+} -doped sample would be much higher (7.1 emu/g) than measured (2×10^{-2} emu/g) if all Fe^{3+} ions participate in FM ordering. The reduction in magnetization is possibly due to the presence of nearby Fe ions which, in the absence of oxygen vacancy, can interact antiferromagnetically by the

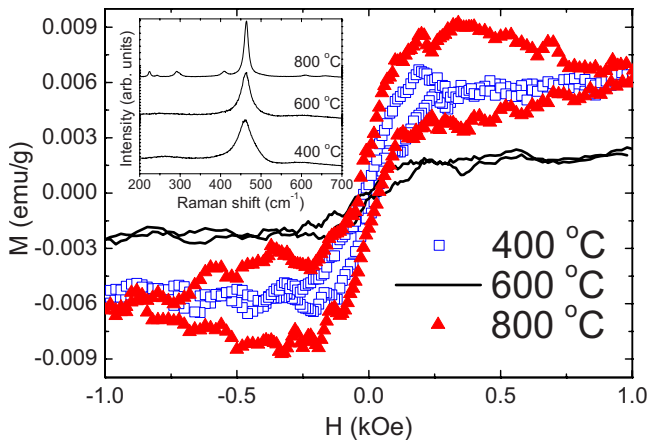


FIG. 4. (Color online) M-H curves of the $\text{Ce}_{0.88}\text{Fe}_{0.12}^{3+}\text{O}_2$ annealed sample. The inset shows room-temperature Raman spectra of the annealed sample.

superexchange interaction.^{10,17} Another possible source of antiferromagnetic interaction (AFM) can be an existence of oxygen vacancies with two trapped electrons (F^0 centers). These vacancies are in a singlet state and mediate weak AFM interaction between nearby magnetic dopants.¹⁸ Thus the magnetic behavior of Fe-doped ceria presents a subtle interplay of the competing magnetic interactions: ferromagnetic FCE coupling strongly dependent on the valence state of Fe dopant, AFM interaction and paramagnetism due to the isolated Fe ions randomly distributed in host matrix.

In order to verify that oxygen vacancies, particularly at the surface of Fe-doped nanoparticles, are responsible for the observed RTFM we performed annealing of $\text{Ce}_{0.88}\text{Fe}_{0.12}^{3+}\text{O}_2$ sample at different temperatures (400, 600, and 800 °C) for 4 h in the atmosphere.

From Fig. 4 it is obvious that annealing degrades FM properties. Such a scenario is expected, because with annealing the particles grow and the surface to volume ratio decreases followed by decrease in V_0 concentration. Hence, oxygen vacancy induced FM ordering should be weakened. With further temperature increase up to 800 °C there is a slight increase in magnetization but still much lower than in unannealed sample (Fig. 3). The explanation can be found in the room temperature Raman spectra of annealed sample shown in the inset. The Raman spectra at 400 and 600 °C clearly show that the annealed sample is solid solution composed of bigger particles. This can be deduced from the shift in the F_{2g} mode to higher energy, decrease in bandwidth and loss of asymmetry on the lower energy side characteristic for small nanoparticles. In the Raman spectrum at 800 °C there are significant changes. Beside the F_{2g} mode which is almost of Lorentzian type profile additional modes appeared and are ascribed to hematite.¹⁵ This implies that the phase segregation took place at this temperature, i.e., majority of Fe atoms

come out from ceria lattice and get converted to $\alpha\text{-Fe}_2\text{O}_3$. The intensity of oxygen vacancy mode decreases with increasing temperature and at 800 °C this mode disappears.

In summary, a series of pure and solid solutions of $\text{Fe}^{2+(3+)}$ -doped CeO_2 nanocrystalline powders are synthesized by SPRT method. As-prepared samples exhibit RTFM which drastically increases with changing the valence state of Fe dopant. Raman measurements demonstrated strong electron-molecular vibration coupling in Fe^{3+} -doped sample due to the excess of additional charge followed by an increase in oxygen vacancy concentration. The ferromagnetic ordering through FCE mechanism, in which oxygen vacancies and TM dopants are involved, degrades with annealing. Our results indicate that the RTFM in Fe doped samples is oxygen vacancy mediated FM strongly dependent on the valence state of Fe dopant.

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