Effect of Fe$^{2+}$ (Fe$^{3+}$) Doping on Structural Properties of CeO$_2$ Nanocrystals

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We have measured the Raman scattering and magnetization of pure and Fe$^{2+}$ (Fe$^{3+}$) doped CeO$_2$ nanopowders at room temperature. The Raman scattering spectra revealed the existence of CeO$_2$ fluorite cubic structure for all investigated samples. The Raman active mode at about 600 cm$^{-1}$, seen in all samples, can be ascribed to the CeO$_2$ intrinsic oxygen vacancies. Additional Raman modes at 720 cm$^{-1}$, 1320 cm$^{-1}$ and 1600 cm$^{-1}$, which appear in the spectra of doped samples, can be assigned to maghemite ($\gamma$-Fe$_2$O$_3$) cation deficient structure, to 2$\omega$CeO$_2$ IR-allowed overtone and two magnon structure, respectively. This implies that our powders are composed of mixed valence states and have defective structure. Presence of oxygen defect states and magnetic ions can be responsible for the observed ferromagnetism at room temperature in both pure and Fe doped samples.

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1. Introduction

Nanostructured CeO$_2$ based materials have reached significant impact in practical applications due to general improvement of catalytic [1], electrical [2], optical [3] and electro-optical [4] properties. Technology of solid oxide fuel cells is currently the most relevant field where CeO$_2$ found applications [5].

Various methods of preparation, such as sol-gel [4], spray pyrolysis [6], sputtering [3], have been used to obtain nanosized CeO$_2$. One of the major challenges for the preparation of these nanostructured oxides is precise control of particle size. In our recent studies [7–9], nanoparticles of CeO$_2$ doped with Nd, Y, and Ba were prepared with self-propagating room temperature (SPRT) synthesis. With this cost and time effective method we were able to produce nanocrystalline materials with an average particle size below 10 nm. CeO$_2$ nanocrystals doped with 3d elements such as Fe, were obtained for the first time by this method of preparation.

Vibrational properties of nanocrystalline systems are dependent on the reduction of crystallite size. Room temperature Raman scattering measurements of CeO$_2$ nanoparticles revealed that the energy of the $F_{2g}$ Raman active mode decreases and the line width increases followed by an asymmetrical broadening with decreasing particle size [10]. Several factors as inhomogeneous strain, phonon confinement, particle size distribution and the presence of defect states were considered to explain such changes [7].

The magnetic properties of CeO$_2$ nanocrystals have been the subject of several studies [11, 12]. The existence of room temperature ferromagnetism in CeO$_2$ nanoparticles is discovered recently whereas bulk counterpart are diamagnetic. It is assumed that the origin of ferromagnetism may be the exchange interactions between unpaired electron spins arising from oxygen vacancies presented at the surfaces of nanoparticles [11].

In the present work, we used Raman scattering and magnetic measurements to determine the effect of Fe$^{2+}$ and Fe$^{3+}$ doping on structural and magnetic properties of CeO$_2$ nanocrystals.

2. Experiment

Nanocrystalline Ce$_{1-x}$Fe$_{2+}$ (Fe$_{x}^{3+}$)O$_{2-y}$ ($x = 0.12$ and 0.06) samples were prepared by the SPRT synthesis using metal nitrates and sodium hydroxide as the starting materials. The synthesis involves hand-mixing of starting materials in alumina mortar for 5–7 min until the mixture gets light brown. After being exposed to air for three hours, the mixture was suspended in water. Rinsing out of reaction byproduct (NaNO$_3$) was performed by centrifuge Centurion 1020D at 3500 rpm. This procedure was performed three times with distilled water and twice with ethanol. The Fe$^{2+}$ doped solid-state solution was obtained according to reaction

\[ [(0.88)\text{Ce(NO}_3)_3 \cdot 6\text{H}_2\text{O} + (0.12)\text{Fe(NO}_3)_3] + 6\text{NaOH} + (1/y)\text{O}_2 \]

\[ \rightarrow 2\text{Ce}_{0.88}\text{Fe}_{0.12}\text{O}_{2-y} + 6\text{NaNO}_3 + 9\text{H}_2\text{O}, \]

(1)

whereas Fe$^{3+}$ doped solid state solution was obtained according to reaction

\[ \rightarrow 2\text{Ce}_{0.88}\text{Fe}_{0.12} \cdot (0.06)\text{O}_{2-y} + 6\text{NaNO}_3 + 9\text{H}_2\text{O}, \]

(2)

\[ \rightarrow 2\text{Ce}_{0.12}\text{Fe}_{0.88} \cdot (0.06)\text{O}_{2-y} + 6\text{NaNO}_3 + 9\text{H}_2\text{O}, \]

(3)

\[ \rightarrow 2\text{Ce}_{0.12}\text{Fe}_{0.88} \cdot (0.06)\text{O}_{2-y} + 6\text{NaNO}_3 + 9\text{H}_2\text{O}, \]

(4)

\[ \rightarrow 2\text{Ce}_{0.12}\text{Fe}_{0.88} \cdot (0.06)\text{O}_{2-y} + 6\text{NaNO}_3 + 9\text{H}_2\text{O}, \]

(5)

\[ \rightarrow 2\text{Ce}_{0.12}\text{Fe}_{0.88} \cdot (0.06)\text{O}_{2-y} + 6\text{NaNO}_3 + 9\text{H}_2\text{O}, \]

(6)

\[ \rightarrow 2\text{Ce}_{0.12}\text{Fe}_{0.88} \cdot (0.06)\text{O}_{2-y} + 6\text{NaNO}_3 + 9\text{H}_2\text{O}, \]

(7)

\[ \rightarrow 2\text{Ce}_{0.12}\text{Fe}_{0.88} \cdot (0.06)\text{O}_{2-y} + 6\text{NaNO}_3 + 9\text{H}_2\text{O}, \]

(8)

\[ \rightarrow 2\text{Ce}_{0.12}\text{Fe}_{0.88} \cdot (0.06)\text{O}_{2-y} + 6\text{NaNO}_3 + 9\text{H}_2\text{O}, \]

(9)

\[ \rightarrow 2\text{Ce}_{0.12}\text{Fe}_{0.88} \cdot (0.06)\text{O}_{2-y} + 6\text{NaNO}_3 + 9\text{H}_2\text{O}, \]

(10)
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2[(0.88)Ce(NO$_3$)$_3$·6H$_2$O + (0.12)Fe(NO$_3$)$_3$·6H$_2$O] +6NaOH + (1/2 - y)O$_2$

→ 2Ce$_{0.88}$Fe$_{0.12}$O$_{2-y}$ + 6NaNO$_3$ + 15H$_2$O. (2)

Unpolarized Raman scattering measurements were performed in the backscattering configuration using micro-Raman Jobin Yvon T64000 system. As an excitation source 514.5 nm line of Ar$^+$ laser was used. In order to avoid sample heating we used very low laser power on the sample (0.24 mW).

Magnetic moment measurements at room temperature were performed using vibrating sample magnetometer (VSM 200) of 14 T cryogen free measurement system (Cryogenic Ltd.).

3. Results and discussion

In Fig. 1 we present room temperature Raman spectra of the Ce$_{1-x}$Fe$_{2+}$+(Fe$_{3+}$)$^+_y$O$_{2-y}$ ($x = 0.12$ and 0.06) samples together with the Raman spectrum of pure nanocrystalline CeO$_2$ sample. The first order $F_{2g}$ Raman active mode of CeO$_2$ nanocrystals appears at 454 cm$^{-1}$. Besides the $F_{2g}$ mode there are additional modes at 600 cm$^{-1}$ and 1048 cm$^{-1}$ which are assigned to intrinsic oxygen vacancies ($V_{Ce^{3+}}$) [7] and the second order Raman mode at X-point of the Brillouin zone [13], respectively.

In the Raman spectrum of Fe$^{2+}$ doped sample (Ce$_{0.88}$Fe$_{0.12}$O$_{2-y}$), the $F_{2g}$ mode is located at nearly the same frequency as the $F_{2g}$ mode of pure CeO$_2$ nanocrystalline sample, with slightly increased line width. Beside the $F_{2g}$ and oxygen vacancy modes, a weak band appears at 720 cm$^{-1}$ (marked with * in Fig. 1), which is assigned to maghemite ($\gamma$-Fe$_2$O$_3$) cation deficient structure [14]. $2\omega_{LO}$ (IR-active) overtone, characteristic for hematite ($\alpha$-Fe$_2$O$_3$), appears at 1320 cm$^{-1}$ [14]. The appearance of modes characteristic for different iron oxide crystal structures can be a consequence of oxidation of mixed valence iron oxide (magnetite Fe$_3$O$_4$), probably caused by laser irradiation.

In the Raman spectrum of Fe$^{3+}$ doped sample (Ce$_{0.88}$Fe$_{0.12}$O$_{2-y}$), the $F_{2g}$ mode is shifted to lower energies and is broader than in the spectra of pure, Fe$^{2+}$ and Fe$^{2+}$/Fe$^{3+}$ ceria doped samples. Red shift and broadening of the $F_{2g}$ mode can be ascribed to the size and strain effects [7, 10] or can be a consequence of electron molecular vibrational coupling due to the increased concentration of defects in oxygen sub-lattice of CeO$_2$ and presence of magnetic ions in ceria lattice.

The intensity of intrinsic oxygen vacancy Raman active mode ($V_{Ce^{3+}}$) in Ce$_{0.88}$Fe$_{0.12}$O$_{2-y}$ sample is more pronounced than in other samples. Such behavior confirms our previous statement that incorporation of trivalent iron in ceria lattice provokes a formation of more defective structure, i.e. higher concentration of oxygen vacancies is formed with Fe$^{3+}$ doping. The Raman active mode at 1320 cm$^{-1}$ can be assigned to $2\omega_{LO}$ IR-allowed overtones of Fe$_2$O$_3$, whereas a weak structure at about 1600 cm$^{-1}$ can be ascribed to two-magnon peak of Fe$_2$O$_3$ phase [14].

In Fig. 1 there are also shown the Raman spectra of mixed valence Fe-doped ceria sample (Ce$_{0.88}$Fe$_{0.06}$Fe$_{0.06}$O$_{2-y}$). The frequency of the $F_{2g}$ mode, for this sample, lies between the $F_{2g}$ values for Fe$^{2+}$ and Fe$^{3+}$ doped samples. The intensity of $2\omega_{LO}$ IR-allowed overtone and two magnon mode of Fe$_2$O$_3$ in this sample is significantly higher than in (Ce$_{0.88}$Fe$_{0.12}$O$_{2-y}$) sample. The appearance of iron oxide Raman modes implies high structural disorder in this sample.

Interesting feature in the Raman spectra of all doped samples, is a mode located at about 830 cm$^{-1}$, which is not observed in the spectra of pure CeO$_2$. This mode is characteristic for adsorbed oxygen species on the surface of CeO$_2$ nanoparticles [15] suggesting that doping with iron can lead to better chemical activity of ceria nanoparticles.

In Fig. 2 there is shown magnetization versus magnetic field for polycrystalline and nanocrystalline CeO$_2$ samples, measured at 300 K. The bulk sample shows a weak diamagnetic response, as it can be expected for CeO$_2$ with Ce$^{4+}$ ions in the $f^0$ electronic configuration. On the other hand, CeO$_2$ nanocrystals show weak ferromagnetic behavior. It has been observed that nonmagnetic oxides at room temperature become weakly ferromagnetic when the samples are in the form of small nanoparticles [11, 12] or very thin films [16].

It was suggested that the origin of this ferromagnetism may be exchange interaction between unpaired electron spins arising from oxygen vacancies formed at surface of nanoparticles [16, 11]. We believe that $f^0$ unpaired electron spins in Ce$^{3+}$, formed at nanoparticles surface, are responsible for room temperature ferromagnetism in nano CeO$_2$. Saturation magnetization of our CeO$_2$ nanocrystals is about 0.0055 emu/g which is comparable with previous results [11, 12].
In Fig. 3 there is shown magnetization versus magnetic field for the Ce\(_{1-x}\)Fe\(_{2+}\)(Fe\(_{3+}\))O\(_{2-y}\) (\(x = 0.12\) and 0.06) samples, measured at 300 K. It can be seen that Fe-doped CeO\(_2\) samples show paramagnetic response with small ferromagnetic component in these samples. The ferromagnetic component only, obtained by subtracting the linear paramagnetic background from \(M(H)\) curves in Fig. 3 is given in Fig. 4. The hysteresis loop for the Fe\(^{2+}\)/Fe\(^{3+}\) doped sample (Fig. 4) is between the loops for Fe\(^{2+}\) and Fe\(^{3+}\) doped samples. Saturation magnetizations (at 10 kOe) can be roughly estimated to be 0.009, 0.014 and 0.018 emu/g for the Fe\(^{2+}\), Fe\(^{2+}/\)Fe\(^{3+}\) and Fe\(^{3+}\) doped samples, respectively. This means that the value of saturation magnetization for the sample doped with Fe\(^{2+}\), Fe\(^{3+}\) is roughly in the middle between the values of saturation magnetization for Fe\(^{2+}\) and Fe\(^{3+}\) doped samples, i.e. saturation magnetization of this ferromagnetic component increases with the increase of oxidation state of Fe dopant.

As we already mentioned the existence of Ce\(^{3+}\) states may be the origin of room temperature ferromagnetism in nano CeO\(_2\). The exchange interaction between 4f\(^1\) nonpaired electrons in Ce\(^{3+}\) can result in weak ferromagnetism experimentally found in nano CeO\(_2\) (see Fig. 2). By doping with Fe we can expect different behavior in the case of 2+ and 3+ valence state. Iron has 3d\(^6\) + 4s\(^2\) valence electrons. In the case of low spin state of Fe\(^{2+}\) ions all 3d\(^6\) ions are compensated (↑↓↑↓↑↓, \(S = 0\)) and they do not contribute to the total magnetic moment of nanoceria. In this case iron as dopant produces higher disorder in ceria structure i.e. an increase of oxygen vacancy concentration which further increases the Ce\(^{3+}\) ion concentration. In this way, the ferromagnetic exchange interaction is also stronger and magnetization saturation value in Fe\(^{2+}\) doped sample is a little bit higher than in pure nano CeO\(_2\) (see Fig. 2 and Fig. 4). In Fe\(^{3+}\) doped samples, 3d\(^5\) electrons in the low spin state can participate in ferromagnetic ordering (↑↓↑↓↑, \(S = 1/2\)). In this case, both Fe\(^{3+}\) and Ce\(^{3+}\) electron spins contribute to ferromagnetic ordering. Consequently, we can expect dramatic increase in magnetization of Fe\(^{3+}\) doped sample, which is experimentally observed in Figs. 3 and 4. In such a way we concluded that the existence of both Ce\(^{3+}\)–oxygen vacancies complexes and Fe\(^{3+}\) ions in the low spin state contribute to the weak ferromagnetism in nanoceria and not only oxygen vacancies as previously stated [11, 16].

4. Conclusion

Nanocrystalline Ce\(_{1-x}\)Fe\(_{2+}\)(Fe\(_{3+}\))O\(_{2-y}\) (\(x = 0.12\) and 0.06) samples were synthesized by self propagating room temperature synthesis method. Raman spectroscopy at room temperature was applied to determine the influence of Fe\(^{2+}/\)Fe\(^{3+}\) doping on structural and vibrational properties of cerium dioxide nanopowders. Doping with trivalent iron causes redshift and broadening of the \(F_{2g}\) mode.
as a consequence of electron molecular vibrational coupling due to the increased concentration of Ce$^{3+}$–oxygen vacancies complexes and magnetic Fe$^{3+}$ ions. The existence of second order Raman modes characteristic for iron oxide suggest that there is a high structural disorder in our samples. From magnetic measurements it was established that nanocrystalline CeO$_2$ sample exhibit ferromagnetic behavior at room temperature. The Fe-doped ceria samples also exhibit small ferromagnetism at room temperature. The saturation magnetization in all doped samples is higher than in pure ceria and increases with an increase of oxidation state of Fe dopant. The presence of Ce$^{3+}$ and Fe$^{3+}$ spin electrons is responsible for observed ferromagnetism.

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References