Journal of Magnetism and Magnetic Materials 464 (2018) 11–17

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Research articles

Spectroscopic investigation of the correlation between localization of electrons and ferromagnetism in CeO_2 nanoparticles

William Lee[a], Shih-Yun Chen[a,*], Eric Nestor Tseng[a], Alexandre Gloter[b,*], Cheng-Wei Ku[a], Xiao-Yan Li[b]

[a] Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan
[b] Laboratoire de Physique des Solides, Université Paris Sud 11, CNRS UMR 8502, F-91405 Orsay, France

A B S T R A C T

Presence of oxygen vacancy (V_O) and the subsequent redistribution of electron are critical in the formation of ferromagnetism in oxides without magnetic impurities. However, the roles play by electron with diverse localization state in magnetism is still unclear. In this study, different V_O related defect complex was obtained in CeO_2 nanoparticles (NPs) by doping various content of Pr^{3+} and performing subsequent annealing process. Room temperature ferromagnetism was observed in all NPs. Combined systematic spectroscopy and microscopy analysis, it is demonstrated that magnetic behavior was strongly correlated to differences in electron localization. Two types of electron localization were revealed, which both result in the reduction of Ce ion. One is localized at the Ce ion adjacent to V_O, while the other distributes at farther shell. Ce^{3+} formed by the later one was found to play the major role in ferromagnetism. To estimate the amount of ferromagnetic active Ce^{3+} ion, a normalization method was proposed based on Raman and X-ray absorption spectroscopy analysis and has been proven to be valid for several systems, including un-doped and doped with Y/Pr/Sm CeO_2 NPs.

1. Introduction

Diluted magnetic semiconductors (DMS) have been developed for years, but with the wide gap between the Curie temperature (T_C) and room temperature, it has been difficult to apply in spintronic devices. Until Matsumoto et al. and Dietl et al. theoretically predicted that room temperature ferromagnetism (RTFM) can be obtained in semiconductors such as ZnO and GaN, great attentions has been attracted in the field of DMS [1,2]. Numerous studies have been invested in unraveling the mechanism of ferromagnetism exchange as well as enhancing the magnetic saturation. Among these, it is now well accepted that the formation of RTFM is correlated to the presence of defects in metal oxide [3–5].

Among metal oxides possess RTFM, CeO_2 has attracted increasing attentions in these recent years. An interesting character of CeO_2 is that it can have a stable structure far from the stoichiometric proportions of oxygen. Therefore, CeO_2 is known to be one of the most appropriate materials to investigate defect-related applications. There are several ways to introduce V_O into ceria. One is doping with trivalent element, the replacement of Ce^{4+} ion by the dopant results in creation of one V_O. Annealing in reducing atmosphere has also been proven to be effective in the formation of V_O in ceria due to its excellent catalyst characteristic. Once V_O forms, the unoccupied 4*f* orbitals of Ce^{4+} will be then filled by electrons, reducing Ce^{4+} ion to Ce^{3+} ion.

Notably, the unpaired electron in the 4*f* orbital of Ce^{3+} has been demonstrated to be one of the origins of ferromagnetism. However, different groups have demonstrated that magnetization was not directly correlated to the amount of Ce^{3+}. Both the distribution of Ce^{3+} and the ratio of Ce^{3+}/Ce^{4+} was found to affect the magnetization [6,7]. Relevant models have been developed to explain the formation of ferromagnetism in oxides for the past decades, including the bound magnetic polarons (BMPs) model developed by Coey et al. with the subsequent F-center exchange (FCE) [4], the charge transfer mechanism [8] and more recently a collective magnetic response in a coherent mesoscopic domain [9]. All these models are based on occurrences of new electronic states, related to the interplay between V_O, excess charge and a defective structure (surface, impurities, etc.). Thus the identification of electronic structure of Ce ion with different structure is necessary in magnetic behavior interpretation.

In this study, different types of V_O related defects were introduced into CeO_2 nanoparticles (NPs) by doping with different content of Pr^{3+} (from 0 to 15%) and perform annealing process. Among the non-magnetic elements with trivalent state, Pr is a suitable candidate to dissolve in CeO_2 since its ionic radii is similar to Ce [10–12]. Defect

* Corresponding authors.
E-mail address: sychen@mail.ntust.edu.tw (S.-Y. Chen).

https://doi.org/10.1016/j.jmmm.2018.05.031
Received 26 January 2018; Received in revised form 3 April 2018; Accepted 11 May 2018
0304-8853/ © 2018 Elsevier B.V. All rights reserved.

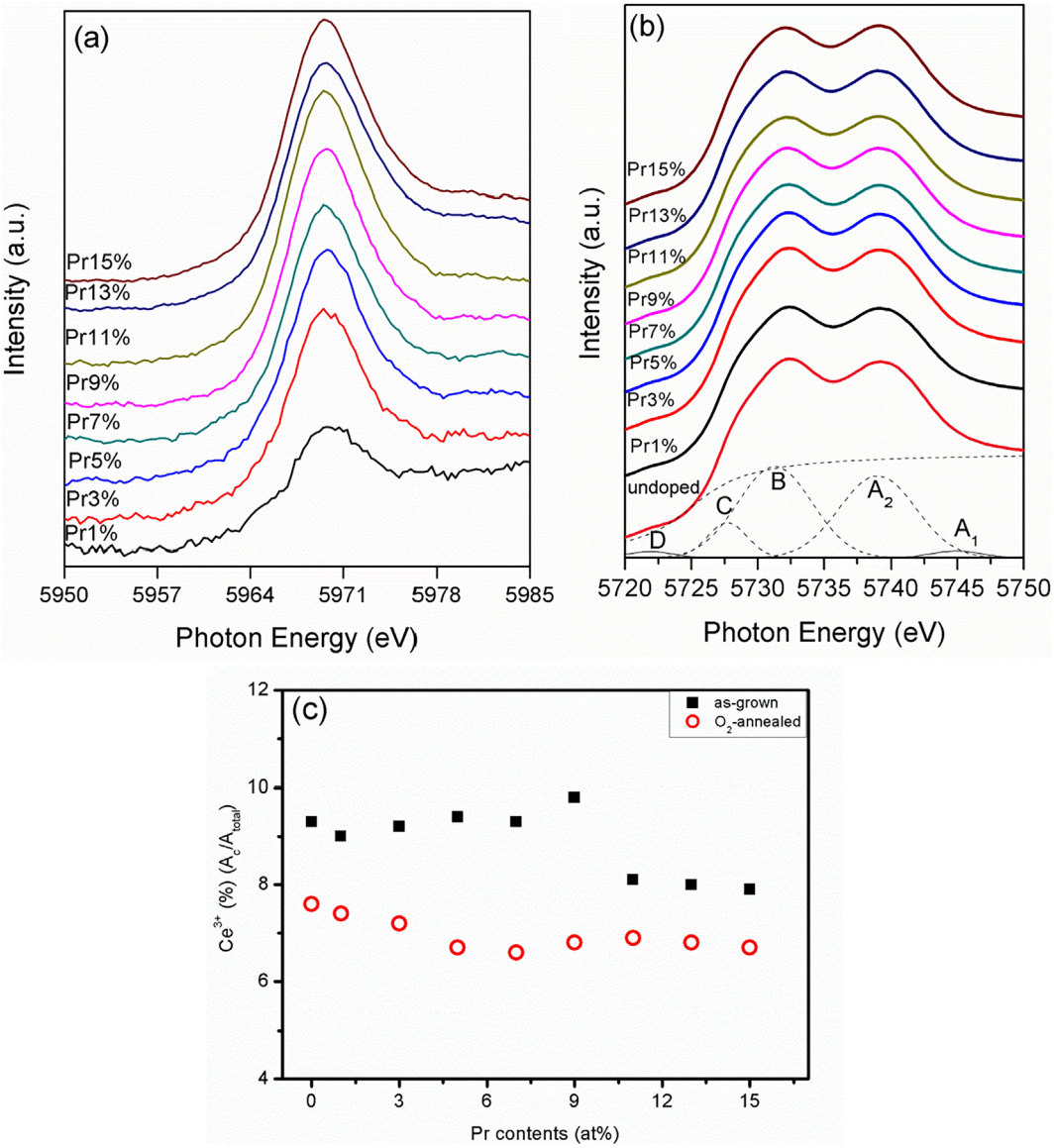

Fig. 1. (a) Pr L-edge of as-grown Pr-doped CeO_2, (b) Ce L-edge of as-grown Pr-doped CeO_2, (c) C^{Ce3+} of CeO_2 NPs doped with various contents of Pr as well as different treatment.

structures were investigated by utilizing X-ray absorption spectroscopy (XAS), Raman spectroscopy and scanning transmission electron microscopy/ electron energy loss spectroscopy (STEM/EELS). The correlation between electron localization and magnetism was revealed. The mechanism of RTFM was explained successfully by a normalization method which was proposed based on Raman and XAS analysis to estimate the amount of ferromagnetic active Ce^{3+} ions. This mechanism was also checked for other ceria NPs, including Y and Sm doped systems, whose microstructures have been reported previously [13,14].

2. Experimental procedures

The starting precursors were $Ce(NO_3)_3{\cdot}6H_2O$ (Alfa Aesar, 99.5%) and various amounts of $Pr(NO_3)_3{\cdot}6H_2O$ (Alfa Aesar, 99.9%), stirred 600 rpm at room temperature with 80% Ethylene Glycol (EG)/Water in a three-necked round bottom flask. 3 Molar NH_4OH was added after the precursor was completely dissolved. The solution was kept at 60 °C for 21 h. The precipitates were subsequently separated by centrifugation at 6000 rpm for 15 min and washed using DI water and alcohol several times. The as-grown CeO_2 NPs were then annealing in O_2 at 300 °C for 2 h.

Raman spectra of the CeO_2 NPs were recorded using a micro-Raman system (Uni-RAM system) and a diode laser at an excitation wavelength of 785 nm. The X-ray absorption near-edge fine structure (XANES) measurements at Ce *L*-edge and Pr *L*-edge were measured by Wigger beamline 17C by using the fluorescence yield mode at room temperature. The monochromator Si (1 1 1) crystals were used in Wiggler beamline 17C with an energy resolution $\Delta E/E$ better than 2×10^4. X-ray magnetic circular dichroism (XMCD) was measured at Dragon beamline 11A in fluorescence yield mode in an applied alternating magnetic field with a strength of ± 1 T. The monochromator resolving power was $E/\Delta E \sim 10{,}000$, and the extent of circular polarization of the X-rays was ~55%. The energy resolutions were approximately 0.3–0.4 eV. STEM/EELS analysis was done by using a USTEM-NION microscope, and a GATAN EELS modified spectrometer operated at 60 keV in order to limit the beam damage. The magnetization was measured at room temperature by Vibrating Sample Magnetometer (VSM) (Lake Shore 7400 Series).

Download English Version:

https://daneshyari.com/en/article/8152579

Download Persian Version:

https://daneshyari.com/article/8152579

Daneshyari.com