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Study of hyperfine interactions in pure and Co-doped CeO_2 nanoparticles by PAC spectroscopy using ^{111}Cd

M. S. Costa · A. W. Carbonari · J. M. Ramos · G. A. Cabrera-Pasca · M. R. Cordeiro · L. F. D. Pereira · R. N. Saxena

Abstract In this work we have used the Perturbed Angular Correlation (PAC) technique to measure the hyperfine interactions in pure nanostructured (crystallite size around 70 nm) as well as doped with 3d transition metal Co (3 at. %) CeO_2 samples. The PAC measurements were performed at different temperatures between 23 and 527°C. The results did not reveal any evidence of hyperfine magnetic interactions. Spectra obtained presented three major frequencies related to substitutional sites in CeO_2, grain boundary sites and intrinsic defect related sites.

Keywords PAC · Ceria · Hyperfine interactions

1 Introduction

Cerium dioxide (CeO_2) is quite important for the high-technology industry with various applications such as in automotive industry, medicine, oxygen sensors, protectors of the radiation and so on. This material has been studied recently using a variety of techniques [1, 2]. Theoretical work has also been carried out [3]. A case of special interest is that Co-doped Ceria is very attractive for multifunctional spintronic applications. CeO_2 doped with divalent or trivalent ions is a promising electrolyte material for application in solid oxide fuel cells [4–6]. Besides that, CeO_2 is considered as a candidate for replacing silicon dioxide in electronic appliances [7].

2 Experimental procedure

The samples of pure and Co-doped CeO_2 were prepared by the Pechini sol-gel method from pure Ce and Co elements. In this methodology metallic Ce and Co

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M. S. Costa (✉) · A. W. Carbonari · J. M. Ramos · G. A. Cabrera-Pasca ·
M. R. Cordeiro · L. F. D. Pereira · R. N. Saxena
Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, São Paulo, Brasil
e-mail: mscosta@ipen.br, messias@if.usp.br

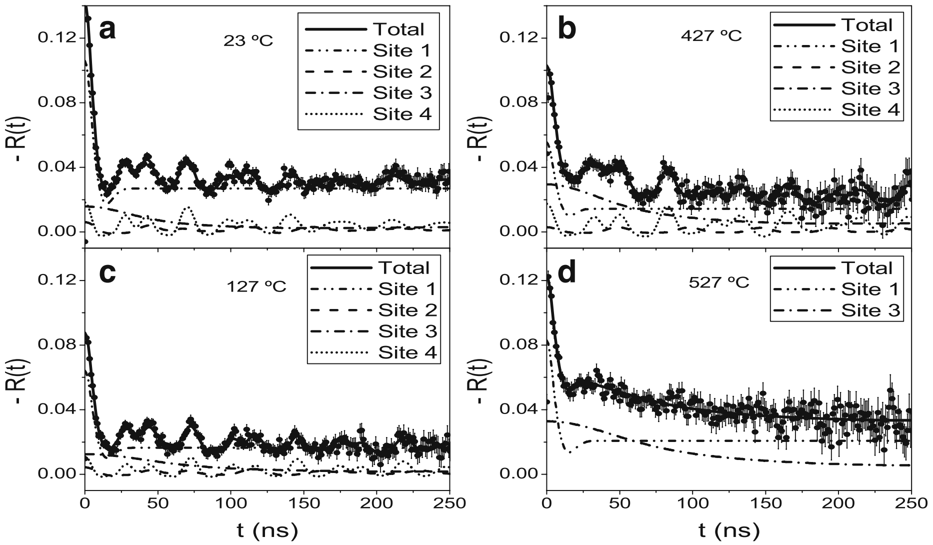


Fig. 1 PAC spectra at indicated temperatures, for ^{111}In-^{111}Cd probe nuclei in pure CeO_2. All data were collected in vacuum, except for 23°C which was collected in air

were separately dissolved in nitric acid and then mixed. The obtained gel was then heated in air in a muffle furnace at 380°C during 10 h. Radioactive probe nuclei $^{111}In \rightarrow ^{111}Cd$ (with known $\gamma - \gamma$ cascade, 171–245 keV) were introduced during the sample preparation in all cases. The obtained pure and Co-doped CeO_2 were annealed at 500°C for 10 h in N_2 or for 8 h in vacuum, as will be mentioned in the next section. The PAC measurements were carried out in the temperature range of 23°C to 527°C with a conventional fast-low coincidence set-up with four conical Baf_2 detectors. A small tubular furnace was used for heating the sample. One set of each sample was prepared following the same procedure used for radioactive samples. These samples were characterized by X-ray Diffraction (XRD), Scanning Electronic Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX).

3 Results

XRD, SEM and EDX results showed the formation of the priority crystalline phase of CeO_2, with mean crystallite size around 70 nm (obtained by means of Scherrer equation) and absence of undesirable elements in the sample.

3.1 Pure cerium oxide

Figure 1 shows the experimental PAC spectra for pure cerium oxide at four different temperatures. All the samples were annealed at 500°C for 10 h in nitrogen atmosphere. Measurements were taken in vacuum, except Fig. 1a that was collected in air. The experimental data were well fitted with four sites, except for 527°C where

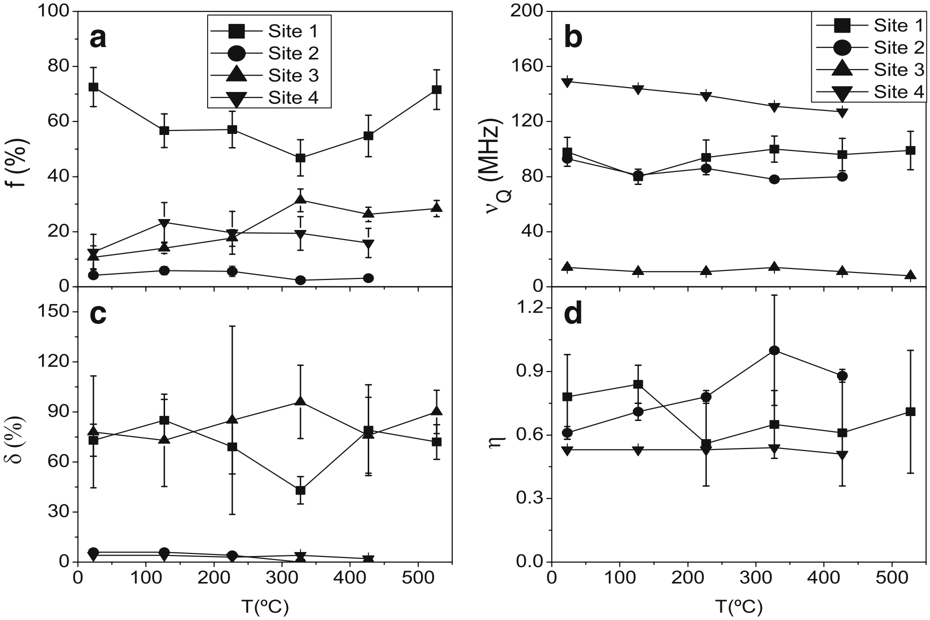
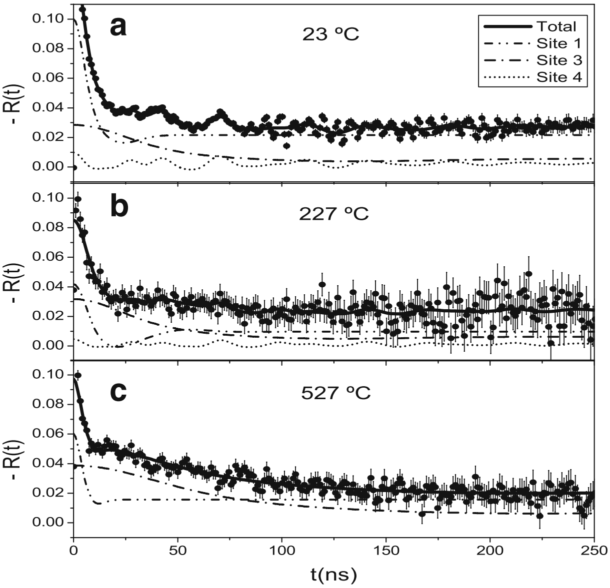


Fig. 2 Experimental data obtained from the PAC spectra presented in Fig. 1. This figure shows: a) fraction f(%); b) quadrupole frequency $\nu_Q(MHz)$; c) frequency distribution paramenter $\delta(\%)$; and d) asymmetry parameter η; versus temperature of data collect

Fig. 3 PAC spectra at temperatures indicated, for trace concentration ^{111}In-^{111}Cd in CeO$_2$ doped with 3% Co. For Fig. 3a sample was annealed at 500°C for 10 h in nitrogen atmosphere and its data were collected in air. The sample of Fig. 3b and c were annealed at 500°C for 8 h in vacuum and their data were collected in vacuum at the temperatures indicated



only two sites appeared. The fit curves corresponding to site 1 are indicated by the dash dot dot, site 2 is presented in dash, site 3 is presented in dash dot, site 4 is presented in dots; and the total curve was designated by the solid line.

Figure 2 shows the experimental data obtained from the PAC spectra for pure cerium oxide presented in Fig. 1. In the figure, site 1 is indicated by the square, site 2 is indicated by the ball, site 3 is indicated by the triangle up and site 4 is indicated by the triangle down.

3.2 Co-doped cerium oxide

Figure 3 shows the experimental PAC spectra for CeO_2 doped with 3% Co at three different temperatures. In Fig. 3a the sample was annealed at 500°C for 10h in nitrogen atmosphere and its data were collected in air at room temperature. The sample of Fig. 3b and c was annealed at 500°C for 8 h in vacuum and their data were collected in vacuum at the temperatures indicated. The experimental data were well fitted with three sites, except for 527°C where only two sites appeared. The curves corresponding to the site 1 are presented in dash dot dot, site 3 is presented in dash dot, site 4 is presented in dots; and the total curve was designated by the solid line. Note that the site 2 presented in dash in undoped cerium does not appear here.

4 Discussion and conclusion

In this work, PAC measurements were carried out at different temperatures between 23–527°C for pure and Co-doped CeO_2 nanocrystalline samples after annealing at 500°C in nitrogen atmosphere or vacuum. In both samples, pure and Co-doped ceria, no relevant ferromagnetic ordering was observed, only the electric quadrupole interaction (characterized by some quadrupole frequency) was observed. The non-observance of ferromagnetic ordering is consistent with experimental work of Liu et al. [8] which reported that ferromagnetism was observed only for sub-20 nm powder. The XRD results showed that mean size of crystallites in our sample is around 70 nm.

For pure ceria, four sites were found for data collected until 427°C, but for 527°C the site 2 and site 4 were vanishing as Figs. 1 and 2 show.

In the work of Wang [9] a fraction of 5–25% of high frequency was also found which was denoted site D, this site disappears above 500°C. The authors suspected that site D is related to a complex of indium with an interstitial cation. The frequency range found in site 4 and its annihilation at 527°C leads us to associate this site to the site D found by Wang.

Sites with wide distribution of frequency are usually related to non-unique crystalline environment. Since our samples are nano-particles and we have observed that site 1 is characterized by a wider distributed frequency, one of the many possible explanations is that this site could be related to probe nuclei that did not diffuse properly throughout the samples, residing instead in sites near the grain boundary.

Site 3 is characterized by a low frequency and null asymmetry parameter ($\eta = 0$). Recognizing that ceria has cubic symmetry, site 3 could be assigned to probe nuclei in substitutional position of cerium in the cube. Previous works in samples that have cubic symmetry [10] also presented low frequencies and small η values. Note that the site 3 fraction increases whereas quadrupole frequency decreases with increasing temperature. Wang found through R(t) spectrum of ceria sample collected at 800°C that the majority of cadmium atoms sit in a cubic environment (zero EFG) as expected for substitutional dopants in a site of cubic symmetry.

Although the fraction for site 2 is rather small, it shows a well-defined frequency, and it was also observed that for Co-doped ceria the site 1, site 3 and site 4 are present, but the site 2 was suppressed as shown Fig. 3. Wang [9] doped samples of ceria with Niobium and found that cerium samples doped with at least 300 ppm Nb/(formula wt.) remove all oxygen vacancies. Although the site 2 was extinct due to doping with cobalt it is, however, difficult to believe that this site is associated with oxygen vacancies because upon doping CeO_2 with Co, which can present as divalent or trivalent ions, an oxygen vacancy should be formed to ensure charge neutrality. More study about it should be carried out to characterize this site. The Figs. 3c and 1d show no difference among pure and Co-doped ceria.

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