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TDPAC measurements in pure and Fe-doped In_2O_3

**C. Sena · M. S. Costa · G. A. Cabrera-Pasca ·
R. N. Saxena · A. W. Carbonari**

Abstract Measurements of the electric quadrupole interactions were used to characterize pure and Fe-doped In_2O_3 samples using perturbed γ-γ angular correlation (PAC) technique with ^{111}In-^{111}Cd radioactive probe. The samples of pure as well as 1 % and 5 % Fe-doped In_2O_3 were prepared by sol–gel method and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive x-ray spectroscopy (EDS). The PAC measurements were carried out with a conventional fast-slow coincidence set-up using four BaF_2 detectors as a function of temperature from 295 K to 1073 K. The powder XRD spectra analyzed with Rietveld method as well as SEM and EDS results showed that Fe-doped samples are homogeneous without any secondary iron oxide phases. The PAC spectra of pure and 1 % Fe-doped In_2O_3 show well-known characteristic quadrupole frequencies for the two non-equivalent sites in the bixbyte structure. The hyperfine parameters in these cases change little with temperature. For the 5 % Fe-doped sample however the PAC spectra changed significantly and a third frequency with large η appears.

Keywords Fe-doped In_2O_3 · PAC spectra · Quadrupole interactions · Bixbyte structure

1 Introduction

Metal-oxide semiconductors such as ZnO, TiO_2, SnO_2 and In_2O_3 have attracted much attention in the recent years due to their electronic and magnetic properties when doped with 3d transition metals. Some of these materials have found

C. Sena (✉) · M. S. Costa · G. A. Cabrera-Pasca · R. N. Saxena · A. W. Carbonari
Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, São Paulo, Brazil
e-mail: cleidilane@ufpa.br

C. Sena
FACET, Universidade Federal do Pará, Campus de Abaetetuba, Abaetetuba, Brazil

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technological applications in electronic and optoelectronic devices as well as gas sensors. Among these metal oxides, In_2O_3 is a promising candidate as a gas sensor because it is a wide band gap (Eg $\sim$ 3.6 eV) n-type semiconductor with cubic bixbyite crystal structure. Different metals such as Ag, Ni, Eu, Gd, Ho have been used as doping agent to improve the properties of In_2O_3 for this application, for example, increase in gas sensor resistance, the sensitivity and stability [1–3]. In an earlier report it has been shown [4] that the addition of Fe ions in the In_2O_3 matrix could modify the crystal structure and optical properties and induce ferromagnetism. Another study [5] has reported the gas-sensitive properties of thin film sensors towards different gases (C_2H_5OH, CH_4, CO, NH_3, NO_2, O_3) based on the double-layer structures such as Fe_2O_3/In_2O_3 and Fe_2O_3-In_2O_3/In_2O_3. The understanding of magnetism in these materials is far from complete and investigations continue. Bérardan and Guilmeau [6] showed that bulk Fe-doped indium oxide samples sintered under argon atmosphere or in air are paramagnetic. The presence of randomly dispersed Fe_2O_3 or Fe_3O_4 clusters of high iron fractions have been linked to super paramagnetic behavior. Singhal et al. [7] believe that the ferromagnetism at room temperature in (5 %) Fe-doped In_2O_3 polycrystalline sample is related to the oxygen vacancies and not related to the presence of impurities or clusters. The discrepancy between the results about the existence of ferromagnetism in thin films or nanocrystalline samples can be related to different surface to volume ratios and therefore to different oxygen vacancy concentrations [7]. In the present work electric quadrupole interactions in the pure and 1 % and 5 % Fe-doped In_2O_3 samples are studied by perturbed gamma-gamma angular correlation (PAC) spectroscopy using ^{111}In-^{111}Cd probe. All samples were prepared by sol–gel method and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS).

2 Experimental procedure

Sol-gel method was used to prepare all samples. The pure metallic In (99.9999 %) and Fe (99.99 %) were separately dissolved in dilute solutions of nitric acid and hydrochloric acid respectively. Citric acid and a few drops of ethylene glycol were mixed with indium nitrate solution to produce pure In_2O_3. Similar procedure, using a mixture of appropriate quantities of indium nitrate and iron chloride solutions was used to produce In_2O_3 doped with 1 % and 5 % Fe. The mixtures were stirred and heated at 353 K until the sol–gel formation. The sol–gel was heated to 673 K slowly to form the powder and pre-calcined for 10 h. The resulting powder was calcined at 973 K for 12 h, pressed into a small pellet and heated again at 973 K for 12 h. The pellets were broken into several pieces and a drop of $^{111}InCl_3$ solution ($\sim$20μCi) was deposited on the surface of the sample sealed in a quartz tube under vacuum and heated at 773 K for 12 h to diffuse the radioactive ^{111}In. The samples were further heated at 973 K for 12 h in air.

The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and perturbed gamma-gamma angular correlation (PAC) spectroscopy. XRD patterns of the samples were obtained with an X-ray diffractometer (X′ PERT) using Cu Kα radiation ($\lambda\alpha_1 = 0.154060$ nm and $\lambda\alpha_2 = 0.154443$ nm) with an operating voltage and current

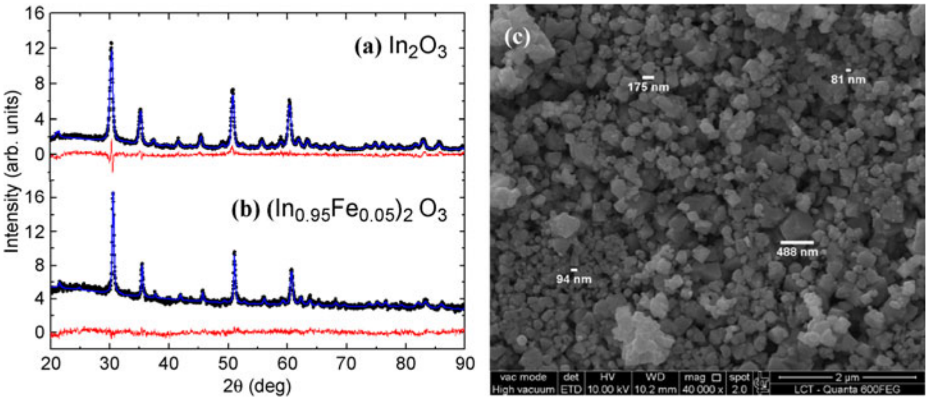

Fig. 1 XRD spectrum of pure (**a**) and Fe-doped (**b**) In_2O_3 powder samples. The *solid lines* represent the calculated pattern using Rietveld method. SEM image of 5 % Fe-doped In_2O_3 (**c**)

of 40 kV and 40 mA respectively. The XRD measurement of Fe-doped as well as pure In_2O_3 powder was carried out after calcination at 973 K and the crystal structure were analyzed by the Rietveld method. The SEM and EDS measurements were also carried out on these samples. The PAC measurements were carried out with a conventional fast-slow coincidence set-up using four BaF_2 detectors as a function of temperature from 295 K to 1073 K.

3 Results and discussions

The XRD spectrum for pure and 5 % Fe doped In_2O_3 are shown in Fig. 1a and b. The diffraction peaks in the curves were fitted and analyzed with Rietveld method to find interplanar distances (d) and full-widths at half height (W) to calculate the lattice parameter (a) and the size of particle (D). The parameters for pure In_2O_3 powder was determined as $a = 1.0151$ nm and $D \sim 30.4$ nm whereas for 5 % Fe doped sample these parameters were found to be $a = 1.0108$ nm and $D \sim 35.4$ nm. The size of particle was calculated from the most intense peaks using the Scherer formula [8]. Both samples formed the cubic structure (space group Ia3) [9]. It was observed that the lattice parameter of 5 % Fe doped sample is somewhat smaller than that of In_2O_3 due to smaller ionic size of dopant Fe compared with In. The SEM images showed that the morphology of $In_{1.95}Fe_{0.05}O_3$ pellet presents the grain size of the order of 80 nm (Fig. 1c). The EDS spectra taken from different regions of the same sample, together with X-ray and SEM results, showed that Fe-doped samples are homogeneous without any secondary iron oxide phases and impurities.

All PAC spectra were analyzed using a model including two or three sites and only pure static quadrupole interactions. No magnetic interaction was observed in any of the Fe-doped samples in the temperature range of measurement. These results thus show that phase with only In_2O_3 structure is present in the samples, and rule out the presence of structure such as Fe_2O_3 (clusters), since these have magnetic character.

The PAC spectra at room temperature in pure In_2O_3 and Fe-doped In_2O_3 (with concentration 1 % and 5 % of Fe) are shown in Fig. 2. Analyses of the PAC

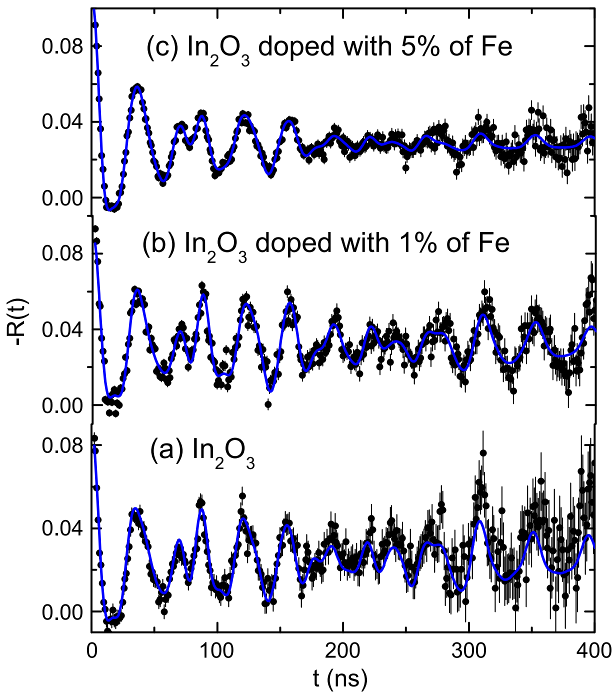

Fig. 2 PAC spectra of pure In_2O_3 pellet and those doped with 1 % and 5 % of Fe at room temperature

spectra of pure and 1 %-Fe-doped samples show the presence of well-known two nonequivalent sites (the *d*-site and the *b*-site) in the In_2O_3 with bixbyte structure. One of the site is assigned to the nuclear probe occupying In atom in the *d*-site with $\nu_{Q1} \sim 117$ MHz, $f_1 = 75$ % and $\eta_1 \sim 0.72$. The other site was assigned to nuclear probes in the *b*-site with $\nu_{Q2} = 152$ MHz, $f_2 = 25$ % and $\eta_2 = 0$. These results are in complete agreement with the earlier results [10, 11]. In the case of the sample doped with 5 % of Fe (Fig. 2c) visible changes are observed in the PAC spectra and it was necessary to fit the experimental data with three sites. The sites 1 and 2 are still observed with same characteristic frequencies and asymmetry parameters but with altered fractional populations. A new third site (f_3) with just about the same frequency $\sim \nu_{Q3} = 152$ MHz as for the site 2 but with large asymmetry parameter ($\eta_3 \sim 0.44$) appears. Table 1 shows the hyperfine parameters for pure and Fe-doped samples for different sites obtained by fitting PAC spectra at room temperature.

Figure 3 shows the PAC spectra and the hyperfine parameters of Fe (5 %) doped In_2O_3 as a function of temperature from 295 K to 1073 K. It can be observed that for site 1 the fractional population (f_1) at room temperature which, diminished from ~75 % for pure In_2O_3 to ~57% when doped with Fe, gradually increases with increasing temperature and recovers its original value of ~75 % at 1073 K. The quadrupole frequency (ν_{Q1}) and asymmetry parameter (η_1) changes very little with temperature. The fractions of site 2 (f_2) and site 3 (f_3) on the other hand decrease gradually with temperature and at 1073 K the sum $f_1 + f_2$ is approximately 25 % same as for the undoped sample at room temperature. From this behaviour we deduce that the site 3 mostly corresponds to the nuclear probe substituting In atoms in the symmetric (*b*-site), but with surroundings somewhat distorted due to

Table 1 Room temperature hyperfine parameters obtained from the fitted PAC spectra of pure as well as 1 % and 5 % Fe- doped In_2O_3 samples

%Fe	f (%)	ν_Q (MHz)	η	δ
Site 1				
0	75 ± 5	117 ± 1	0.72 ± 0.01	0.029 ± 0.002
1	76 ± 5	116 ± 1	0.73 ± 0.01	0.031 ± 0.001
5	57 ± 5	116 ± 1	0.72 ± 0.01	0.048 ± 0.001
Site 2				
0	25 ± 2	152 ± 1	0	0.010 ± 0.003
1	24 ± 1	151 ± 1	0	0.012 ± 0.003
5	9 ± 1	151 ± 1	0	0.013 ± 0.003
Site 3				
0	–	–	–	–
1	–	–	–	–
5	34 ± 2	150 ± 1	0.44 ± 0.01	0.109 ± 0.005

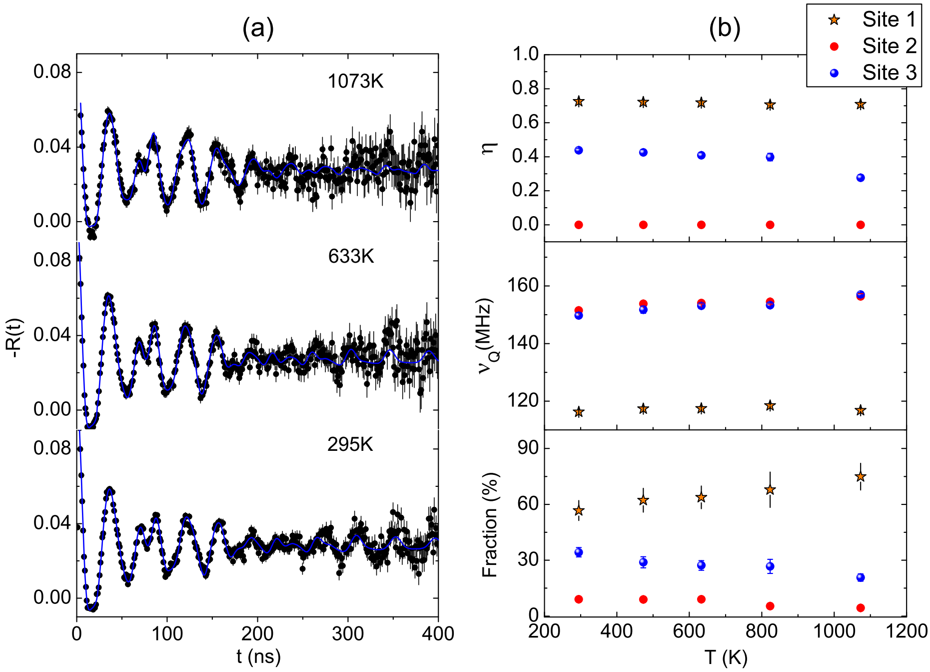

Fig. 3 PAC spectra and their hyperfine parameters (fraction, ν_Q and η) of In_2O_3 pellet sample doped with 5 % of Fe as a function of temperatures

Fe-doping. The result is quite consistent with conclusions of the work of González et al. [12] and Aliabad et al. [13]. The quadrupole frequencies (ν_{Q2}) and (ν_{Q3}) remain practically identical but increase slightly with temperature from ~151 MHz at 295 K to ~156 MHz at 1073 K. While $\eta_2 = 0$ and does not change with temperature, η_3 decreases from ~0.44 at 295 K to ~0.28 at 1073 K.

4 Conclusion

PAC measurements were carried out for pure and Fe-doped In_2O_3 using ^{111}In-^{111}Cd radioactive probe in a temperature range of 295–1073 K. No magnetic interactions were observed in this temperature range. The results were analyzed therefore using a model with pure electric quadrupole interactions. Significant changes in the PAC spectra were observed for In_2O_3 samples doped with 5 % Fe where an additional site with a frequency equal to the second site but more distributed and asymmetry parameter nonzero was observed. This site has been attributed to ^{111}In probe substituting part of In atoms in the symmetric (b-site). It is clear that Fe substitution at 5 % does change the electronic structure of the near neighborhood of this site in In_2O_3. It is however, not possible to conclude that this modification makes this material better suited for applications as gas sensor. Additional measurements of the resistance of pure and 5 % Fe-doped samples are in progress to investigate the possibility of application of these materials as gas sensors.

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