

Investigation of electric quadrupole interaction in TiO₂ by means of perturbed gamma-gamma angular correlation spectroscopy

Thiago Martucci,¹ Juliana Marques Ramos¹, Artur Wilson Carbonari¹, Andréia S. Silva¹ and Rajendra Narain Saxena¹

¹Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
thiagomartucci@yahoo.com.br

ABSTRACT

TiO₂ has called attention in both basic research and technological applications as an energy converter in solar cells, photocatalyst for water purification, sunscreen material, drug detection, and other applications. In addition TiO₂ is a candidate for use in medical devices, food preparation surfaces, air conditioning filters and sanitary ware surfaces. TiO₂ has two crystalline phases: anatase and rutile. The structural properties and hyperfine interactions in TiO₂ were investigated by perturbed gamma-gamma angular correlation (PAC) spectroscopy using ¹¹¹In and ¹⁸¹Hf as probe nuclei.

The PAC spectroscopy provides information on crystalline and electronic structure at an atomic scale. In the present work, PAC measurements on TiO₂ were focused on the development of a methodology to prepare bulk samples, which have been characterized by conventional techniques such as x-ray diffraction, (XRD), scanning electron microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). The samples were prepared by the sol-gel Pechini method. The resulting powders were annealed at different temperatures in a tubular furnace under nitrogen atmosphere. The PAC measurements were carried out at room temperature in air.

The occupation fraction of the probe nuclei reached 50% when the sample was annealed at 1373K and after measured at room temperature. In this case the frequency measured in site 1 is in agreement with that found in literature for substitutional titanium site in rutile structure when ¹¹¹In were used as probe nuclei. It was measured a frequency more closely to that was found in literature[7] for the case in which ¹⁸¹Hf were used as probe nuclei when the sample annealed at 1373 K and measured at 973 K .

1. INTRODUCTION

TiO₂ is a large band gap semiconductor and it has emerged as one of the most important materials with technological applications. Some technological applications that can be cited are: photocatalyst for water purification, sunscreen material for the protection from UV light, white pigment in paint, drugs, lipsticks, toothpaste, energy converter in solar cells.[1]. In addition, TiO₂ is a candidate for use in medical devices, food preparation surfaces, air conditioning filters and sanitary ware surfaces.[5] TiO₂ has two crystalline phases: anatase and rutile.[1]. It was reported that the complete phase transformation from anatase to rutile structure occurs when the sample was annealed at about 1073 K.[2]

Perturbed Angular Correlation (PAC) is a technique used to provide information on electronic and crystalline structures at an atomic scale. In addition, PAC is used to investigate phase transitions in crystals what it was carried out in this present work. This technique is based on implant a radioactive probe nucleus into a well defined site in the crystalline lattice. In PAC measurements, the radioactive decay of the nucleus used as probe takes place through the emission of two successive gamma rays.[3]

The probability of emission of the gamma ray depends on the angle the nuclear spin axis and the direction of emission. When the first gamma ray is emitted, the nucleus reach its intermediate state. This is the probe nucleus used in PAC experiment. Under ordinary circumstances, the radiation pattern of from a radioactive sample is isotropic because the nuclear spins are randomly oriented. In a radioactive sample which decays trough a gamma cascade, a ensemble of nucleus with spins in the same direction are selected. When the first gamma ray is emitted, a nuclei in the intermediate state is formed and its magnetic substates are not equally populated because only some transitions are allowed. Thus the emission pattern is anisotropic. The two gamma rays should measured in coincidence since the detection of the gamma ray determines the selection of an ensemble nuclei with spins in the same direction. This the unperturbed angular correlation.[4]

Emission of the first gamma ray populates a intermediate level and emission of the second gamma ray depopulates this level. During the life time this intermediate level, and with the implantation of the nucleus in the crystalline lattice, the associated nuclear moments interacts with the extranuclear environment. The spatial and temporal correlations between the two gamma rays are changed by hyperfine interaction. In nonmagnetic crystals, the interaction of the nuclear moment of the nucleus with electric-field gradient is measured. In magnetic crystals, the nuclear-magnetic-dipole moment interacts with the magnetic hyperfine field.[3] The perturbed angular correlation is given by:

$$W(\theta, t) = \sum_k G_{kk}(t) A_{kk} P_k \cos(\theta) \quad (1)$$

G_K is the perturbation factor which is given by:

$$G_{kk}(t) = \sum_n S_{kn} \cos(\omega_n t) \quad (2)$$

S_{kn} are the normalized amplitude for each transition frequency.

The equation (1) allow to calculate the electric gradient field in nucleus site and respective asymmetry parameter. The transition frequencies provides information about quadrupolar frequency ν_Q which is given by:

$$\nu_Q = \frac{eQV_{zz}}{h} \quad (3)$$

V_{zz} is the major component of electric field gradient [6]

If the nucleus is subject to a hyperfine interaction, the interaction may cause a change in the population with the time of the magnetic substates until the emission of the second gamma ray. Electric and magnetic fields detection is possible because the nucleus has a electric quadrupole moment and a magnetic dipole moment.[4]

The measurements were taken through a four conical BaF₂ detectors spectrometer in air and at room temperature.

2. EXPERIMENTAL

With the aim of develop a methodology of preparation of bulk samples, doped TiO₂ samples were prepared as follows. The following procedure described is that carried out for ¹¹¹In-doped TiO₂. Highly metallic titanium was dissolved in hot hydrochloric acid during several hours. Citric acid and ethylene glycol were added to the titanium solution which was stirred and dried until the gel was obtained. During this process, ¹¹¹In was introduced in the samples through the addition of about 20 μCi of ¹¹¹InCl₃. The sol-gel obtained was evaporated to dryness on a hot plate at 423 K. After the gel is obtained, the sample was heated in air in muffle furnace at 653 K and a powder is obtained. This is the sol-gel Pechini method. The resulting powder was annealed in temperature range of 773 K-1373 K in a tubular furnace for 10 h under nitrogen atmosphere. In this furnace the diffusion of the ¹¹¹In occurs. Now, it will be described the procedure for ¹⁸¹Hf- doped TiO₂ sample preparation. Highly pure metallic Ti was dissolved in hot hydrochloric acid for several hours. During this process the pH of the solution was controlled with the addition of ammonium hydroxide. In the first addition, the pH increased from 2 to 5 and precipitation was observed. When the temperature increased, the pH reached the value of 14 which dropped to 4 through the addition of hydrochloric acid. With the addition of ammonium hydroxide, the pH reached the value of 7, which remain in this value. Irradiated Hf metal was dissolved in a solution of hydrofluoric acid diluted in deionized water. The resulting solution was added to the titanium solution. After that, citric acid and ethylene glycol were added to the same solution. Through stirring and heating, the gel was obtained after the sample was dried. Then the sample was calcined at 673 K in a muffle furnace and a powder was obtained. The sample was heated at in a tubular furnace at 1373 K under nitrogen atmosphere for 10 h. The sample was measured at 973 K and 1223 K by using the PAC spectrometer.

Now, it will be described the procedure for ¹⁸¹Hf- doped TiO₂ sample preparation. Highly pure metallic Ti was dissolved in hot hydrochloric acid for several hours. During this process the pH of the solution was controlled with the addition of ammonium hydroxide. In the first addition, the pH increased from 2 to 5 and precipitation was observed. The solution was maintained heated at 423K. After some hours, the pH reached the value of 14 which dropped to 4 through the addition of hydrochloric acid. With the addition of ammonium hydroxide, the pH reached the value of 7, which remain in this value. Irradiated pure Hf metal was dissolved in a solution of hydrofluoric acid diluted in deionized water. The resulting solution was added to the titanium solution. After that, citric acid and ethylene glycol were added to the same solution. Through stirring and heating, the gel was obtained after the sample was dried. Then the sample was calcined at 673 K in a muffle furnace and a powder was obtained. A thermal treatment was made at 1373 K under nitrogen atmosphere for 10 h. The sample was measured at 973 K and 1223 K by using the PAC spectrometer

The PAC spectrometer used consist of four conical BaF₂ scintillation detectors with photomultiplier tubes with the necessary associated electronics. When the gamma radiation is detected, two signals are generated: time and energy that are extracted from photomultipliers of the BaF₂ detectors and processed in coincidence unit. In this time scale, the time signals are fast and provide information about the time and the energy signals are slow and provide information about the energy of the emitted gamma rays. This is the experimental set up used to take the measurements in air at room temperature.

The samples annealed at 1273K and 1373K were divided in two parts each one before the insertion of probe nucleus during the preparation procedure of the powder. One part of the two samples without the probe nucleus inserted were characterized by x-ray diffraction. The radiation pattern of the sample annealed at 1273K reveals the complete phase transformation from anatase to rutile structure. PAC measurements were carried out in the samples in which the radioactive probe nucleus were inserted. The probe nucleus used in this measurements was the ^{111}In which decays to ^{111}Cd through the 171-245 keV gamma cascade. The 245 KeV state of ^{111}Cd is the intermediate state and causes a perturbation in the correlation function of the emitted gamma rays which is expressed by perturbation factor $G_{\text{KK}}(t)$, which provides information about hyperfine interactions and allows to determine the nuclear quadrupole frequency ν_0 , the asymmetry parameter η and the major component of the electric field gradient tensor V_{ZZ} in its quantization axis.

3. RESULTS AND DISCUSSION

PAC measurements in a TiO_2 sample sintered at 373K and in TiO_2 samples annealed at 773K, 873K show frequencies with a wider distribution. The frequencies of the samples annealed at 1273K and 1373K are in agreement with the value already measured in literature for rutile. This is the substitutional titanium site found in literature (site 1). [3] In site 2, a major value of frequency was measured. In samples annealed at 1273K and 1373K the distribution frequency is smaller and the occupation fraction in the site 1 increased and reached the value of 50,00%. The frequency in the site 2 is probably due a nuclei that remains in the surface. The frequency of the ^{181}Hf - TiO_2 doped sample measured at 973 K is 810.615 MHz while the frequency found in literature is 829.5156 MHz [7]. The asymmetry parameter values measured in this work are in agreement with that found in literature. When the sample was measured at 1223 K, the frequency measured is 793.097 MHz. Differences in measured frequencies when the ^{181}Hf - ^{181}Ta were used as probe nuclei are probable due the compound used for insertion of the probe nuclei. There are different Hf compounds which forms chemical bounds also different, easier or not to be separated. The annealing temperature can be or not enough to separate the element from Hf. The electric field around probe nuclei is different for each element and therefore the electric interaction is different. In this experiment, the compound HfF_4 was used for the insertion of hafnium nuclei, while in an experiment reported in literature [7], the compound HfCl_4 was used. In this work, the annealing temperature was enough to separate chlorine from hafnium and the measurements were carried out with the Hf nuclei that was not bound to other element. In our experiment, the fluorine atom was not separated from hafnium because the annealing temperature was not enough to separated the chemical bound that is stronger than other. The results of our experiment suggest that electric-field gradient seen by hafnium nuclei is changed due the fluorine atoms which were not separated from hafnium atoms, what therefore interferes in PAC measurements. The values of hyperfine parameters are shown in table bellow. The obtained spectra for each annealing temperature are presented in figures 3, 4, 5 and 6.

Table 1. Hyperfine parameter showed for TiO₂ after measured of PAC.

TiO ₂	¹¹¹ Cd		¹⁸¹ Hf	
	Sample 1 annealed at 1273K	Sample 2 annealed at 1373K	Sample 3 annealed at 973K	Sample 4 annealed at 1223K
Site 1	105.9 MHz	102.7 MHz	810.6 MHz	793.1 MHz
Site 2	199.7 MHz	138.7 MHz	477.6 MHz	360.8 MHz

The X-ray radiation patterns are showed in figures 1 and 2 and reveals that the anatase phase is predominant.

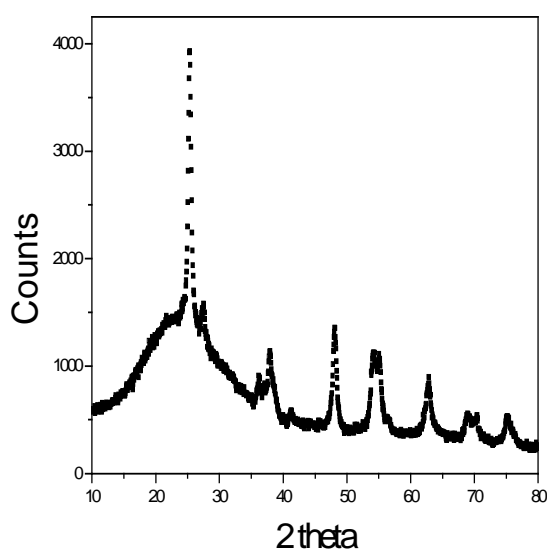


Figure 1. X-ray diffraction pattern of the sample calcined at 653K in a muffle furnace.

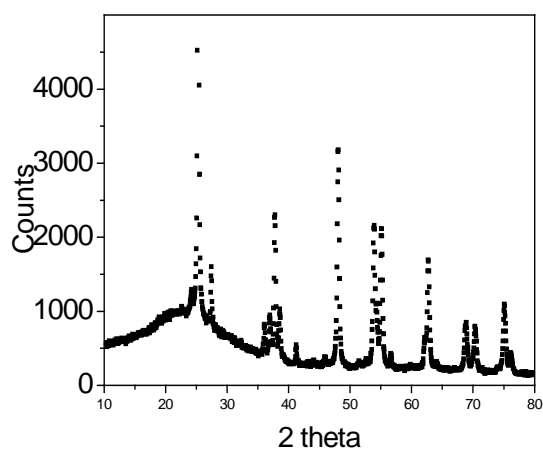


Figure 2. X-ray diffraction pattern of the sample annealed at 973K in a tubular furnace.

PAC measurements are showed in figures 3, 4, 5 and 6.

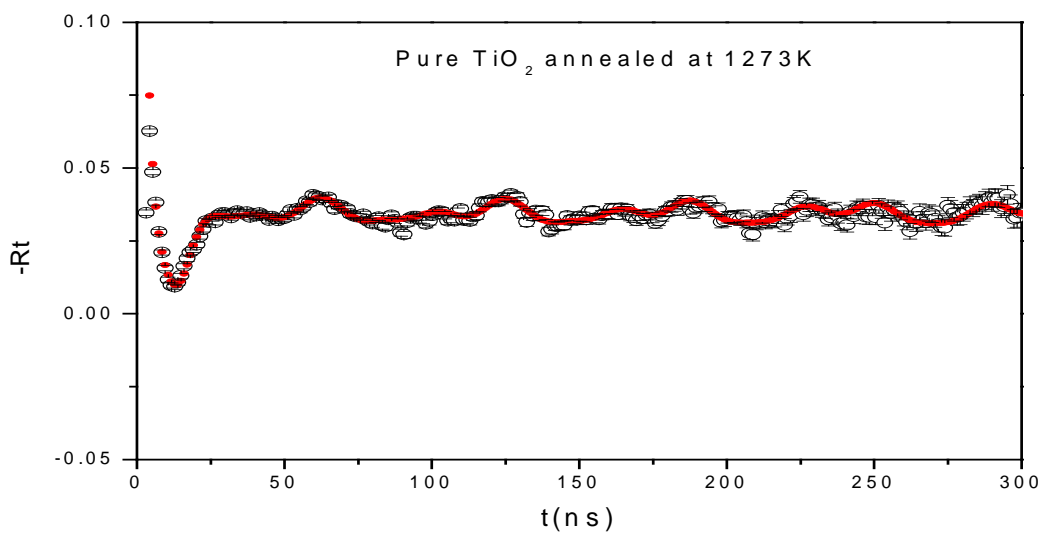


Figure 3. PAC measurements of TiO₂ sample annealed at 1273 K and measured at room temperature using ¹¹¹Cd as probe nuclei.

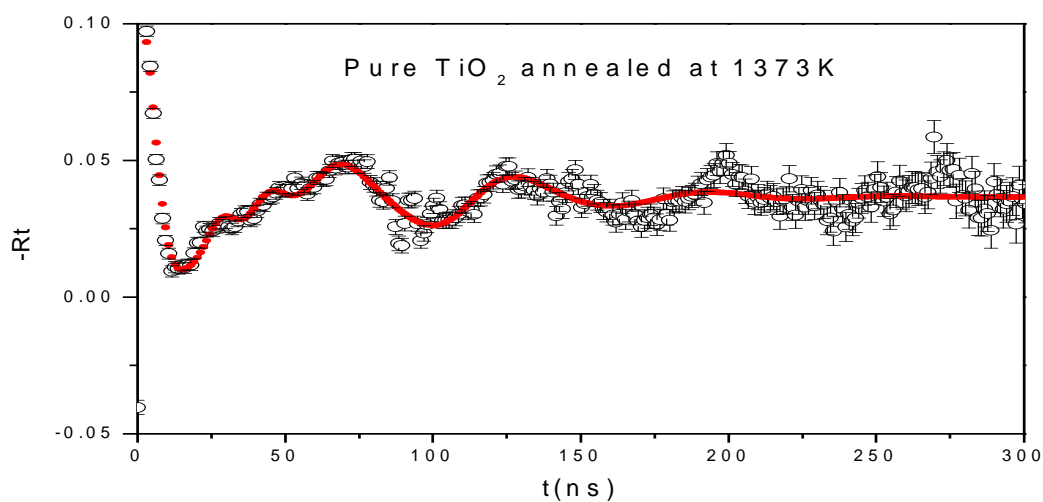


Figure 4. PAC measurements of TiO₂ sample annealed at 1373 K and measured at room temperature using ¹¹¹Cd as probe nuclei.

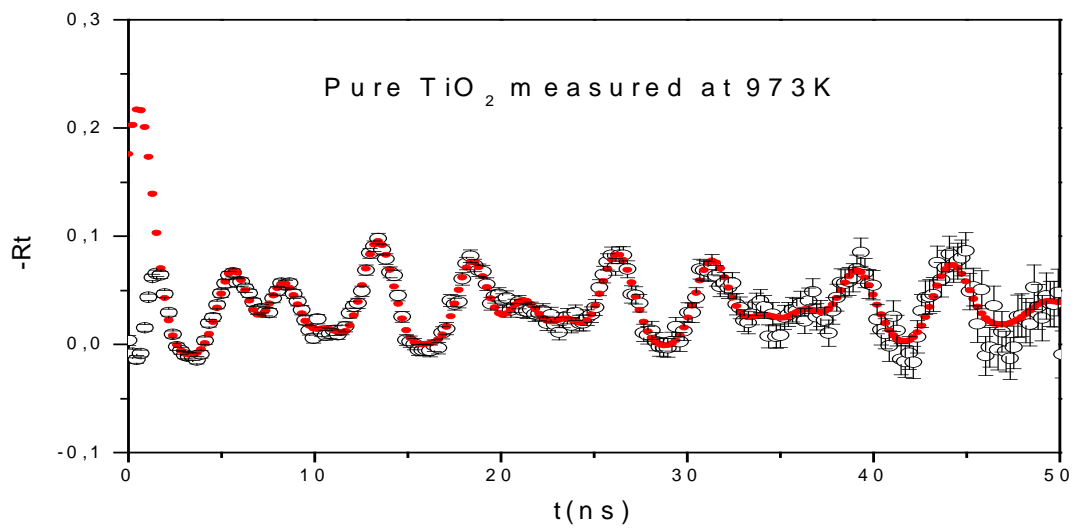


Figure 5. PAC measurements of TiO_2 sample annealed at 1373 K and measured at 973 K using ^{181}Hf as probe nuclei.

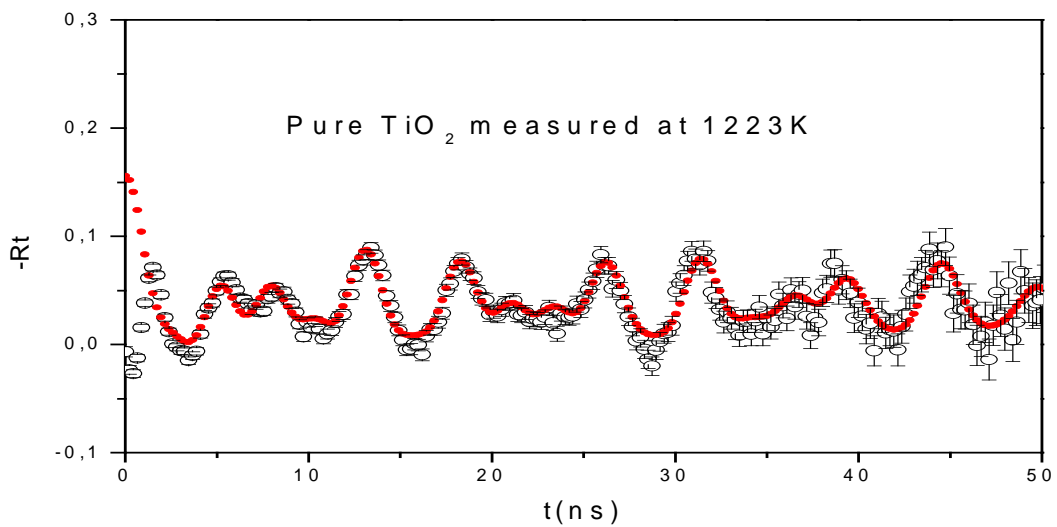


Figure 5. PAC measurements of TiO_2 sample annealed at 1373 K and measured at 1223 K using ^{181}Hf as probe nuclei.

4. CONCLUSIONS

The methodology used to prepare polycrystalline bulk samples reveals to be adequate since we have observed a frequency which are in agreement with that observed in the literature for substitutional titanium site in rutile structure when the sample was annealed at 1373K.[3] This is the frequency observed in site 1. In site 2, other frequency is observed in sample annealed at 1373 K, probably due a interstitial position of the nuclei in rutile structure. Frequencies measured in samples doped with ^{181}Hf - ^{181}Ta are different from those reported in literature probably due the compound used in this work to insert the probe nuclei. HfF_4 was the compound used in this work. Fluorine atoms were not separated from Hf atoms. The results of our experiments suggest that a change in the electric-field gradient seen by hafnium nuclei, interfering in PAC measurements.

ACKNOWLEDGMENTS

Financial support for this research was partially provided by the Comissão Nacional de Energia Nuclear (CNEN). A WC and RNS thankfully acknowledge the support provided by CNPq in the form of research fellowship.

REFERENCES

1. SATYENDRA, K. D; SANJAY,V. T; TILMAN, Butz.. *The nuclear quadrupole interaction at ^{111}Cd and ^{181}Ta sites in anatase and rutile TiO_2 : A TDPAC study. Journal of Physics and Chemistry of Solids*, **70**, pp 778-781 (2009).
2. BAORANG, L; XIAOHUI W;, M. Y, Longtu L. *Preparation and characterization of nano-TiO₂ powder. 78, Materials Chemistry and Physics*, **78**, pp 184-188 (2002).
3. Adams, J. M; Catchen G. L. Catchen; *Physical Review B, Anomalous crystal chemistries of the ^{111}In - ^{111}Cd and ^{181}Hf - ^{181}Ta probes in rutile TiO_2 studied using perturbed-angular-correlation spectroscopy. Brief Reports*,**50 number 2** (1994).
4. Genene T. M. *Indium-impurity pairs in semiconductors and the study of the influence of uniaxial stress on defect complexes in silicon*. 2003. tese (DOUTORADO) Universidade de Bonn.
5. BARLETTA, M; GISARIO A; RUBINO G; TAGLIAFERRI V. *Surface & Coatings Technology*,**201**, pp 3212-3228 (2006).
6. Mercúrio M.E., *Investigação de interações hiperfinas em ZnO e $\text{Zn}_{(1-x)}\text{Co}_{(x)}\text{O}$ pela técnica de Correlação Angular $\gamma - \gamma$ Perturbada*.2009 DISSERTAÇÃO(MESTRADO) –Instituto de Pesquisas Energéticas e Nucleares, São paulo
7. BANERJEE, D.D; THAKARE S.K; NABHIRAJ S.V; MENON P.Y; BHANDARI R.K; KRISHNA K. *Study of surface-bulk mass transport and phase transformation in nano-TiO₂ using hyperfine interaction technique. Journal of Physics and Chemistry of Solids*,**71**,pp 983-987 (2010).