

SYNOPSIS

The topic of the present thesis is mainly divided into two parts:

- a. The development of a fast-slow coincidence setup for the Time Differential Perturbed Angular Correlation (TDPAC) measurements based on $\text{LaBr}_3(\text{Ce})$ detectors.
- b. The hyperfine study of different physico-chemical phenomena related to group-IVB metal oxides using the above TDPAC spectrometer and to envisage the sensitivity of the present nuclear hyperfine technique TDPAC in order to study chemical matrices in atomic level.

The objective of the present work is to perceive the sensitivity and versatility of TDPAC technique in different types of chemical phenomena with an atomic scale resolution. The study is not confined in a particular field of chemical phenomena; rather the wide applicability of the hyperfine technique has been emphasized. For the study with this hyperfine tool, a fast-slow coincidence circuit with a CAMAC-based data-acquisition system has been developed. The latest available $\text{LaBr}_3(\text{Ce})$ scintillation detectors coupled to a fast PM Tube have been used in the above circuit. After coupling the detector-assembly to the coincidence circuit, the characteristics of the detector system has also been studied in order to optimize the best operational condition for the present measurements. This setup was used for the subsequent TDPAC measurements in order to study the different chemical phenomena. For this, group-IVB metal oxides, viz., TiO_2 , ZrO_2 and HfO_2 , have been chosen based on their versatile application of these three oxides. The areas of the study in the present thesis have been chosen on the basis of the applications of these oxides. Further the nuclear probe used in the present study, i.e., ^{181}Hf , falls in the same group and hence, has got the maximum probability to replace the lattice site in any of these three oxides prepared by a soft chemical method along with the probe. The minute changes in the different

chemical phenomena, which otherwise are hardly perceived by any other tool, have been discussed with the help of TDPAC in the present thesis. In some cases, the present work has delivered several new data in the field of TDPAC. Along with the different types of chemical phenomena, the technique has also been used to study the different dimensions (viz., bulk, thin film and nano) of materials. Another aspect of TDPAC, viz., the effect of radioactive decay process feeding the γ - γ cascade has also been studied with $^{111}\text{In}/^{111}\text{Cd}$ probe in case of pure oxides. In some cases, the experimental results have been corroborated by the theoretical calculations of EFG at ^{181}Ta site using Wien2k code.

TDPAC is a nuclear probe technique based on hyperfine interaction. In case of TDPAC, it requires a γ - γ cascade fed by the decay of a parent isotope. The parent isotope is produced by a nuclear reaction and then decays by particle or γ -ray emission to produce the daughter isotope. Then the daughter atom, inside the matrix under study, acts as “wound-up spy” to transfer information of its host matrix while returning to its ground state. The interaction of the nuclear electric quadrupole moment of the intermediate level with an electric field gradient (EFG) leads to a perturbation or attenuation in the angular correlation pattern. The essence of a TDPAC experiment is to extract the TDPAC parameters, viz., the quadrupole frequency, asymmetry of EFG and frequency distribution. Over the other hyperfine techniques, PAC has got some advantages. In PAC, there is no temperature and solid state restriction and so, high-temperature phase transition, solution chemistry of metal complexes and rotational diffusion of macromolecules can be studied by this technique. There is no constraint about the amount of material. In PAC, the probe is added to the matrix in high dilution so that the crystal structure of the matrix under study does not get affected and hence, the same probe can be utilized to study different matrices. PAC has been utilized in the borderline of Physics, Chemistry and Biology. It

has been applied in defect study, surface study, study of phase-transition, solid state reactions, rotational diffusion etc.

In the present thesis, the TDPAC parameters for pure bulk oxides have been measured and then used for all the subsequent measurements. The values for the TDPAC parameters were explained in terms of the crystal structure of the three oxides. The parameters for anatase TiO_2 were measured for the first time by us. In literature, there exists a wide variation in the measured value for quadrupole frequency in case of HfO_2 . Hence the TDPAC parameters for HfO_2 have been remeasured and compared with that for ZrO_2 . The TDPAC parameters also reflect the identical crystal structure for both HfO_2 and ZrO_2 . The optical properties of TiO_2 can be modified by doping with suitable dopant. The role of dopant in the modification of different properties can not be described by any single theory. The study in the atomic scale is required to probe the role of the dopant in modifying the properties of the host matrices. In this motivation, the TDPAC method has been utilized to study the role of Mn and Zr atoms in rutile matrix. One is transition element with different possible valence states and the other is the same group element as Ti. The minute difference in metal-metal interaction in these doped systems could be resolved by TDPAC technique. The other oxide HfO_2 , in its fiber form, is used as the target material for Radioactive Ion Beam (RIB) preparation. For this application, the thermal behavior of the fiber is of major importance. In the present thesis, it has been shown that the high temperature behavior of the fiber material could well be studied by the TDPAC method and the meager loss in crystallinity at 1673K, which could otherwise not be possible to realize, could be distinctly perceived from the measurement of TDPAC parameters. Those parameters are so sensitive to the local environment around the probe atom that any minute change could easily be identified. The effect of γ -irradiation in bulk anatase and rutile structures has also been studied by the TDPAC

technique. Although, these crystal structures are so compact that it is not apparently expected to have any effect of γ -irradiation on these structures, it is a good opportunity to reinvestigate and confirm the present scenario by this hyperfine tool TDPAC.

In case of TiO_2 , anatase and rutile have got their own applications. The mechanism of phase transition from anatase to rutile is of much importance in order to stabilize a particular phase for a specific application. In nano dimension, anatase is used as photocatalyst and photocatalytic efficiency can be enhanced by inserting a nano metal core in nano TiO_2 shell. The mechanism of phase transition in 70nm TiO_2 along with the role of surface to bulk mass transfer has been investigated with this hyperfine tool TDPAC. Again the effect of nano Ag metal core in the above phase transition has been studied by TDPAC method in case of Ag@TiO_2 core-shell nanoparticles. The HfO_2 thin film is presently a leading candidate to replace SiO_2 in gate dielectrics. The thin film of HfO_2 on Si surface is reported to undergo Hf-silicide formation which is of major concern for its application as gate-dielectric. In the present thesis, TDPAC technique has been utilized to the study the evolution of ~ 50 nm Hf thin film on Si(111) surface to the monoclinic HfO_2 phase under 10 mbar O_2 partial pressure. The possibility of Hf-silicide formation has also been revisited by this hyperfine technique.

The work embodied in this thesis has been divided into five chapters:

- Introduction: Group-IVB metal oxides, TDPAC and other complimentary methods.
- Development of Fast-Slow Coincidence Setup with $\text{LaBr}_3(\text{Ce})$ Detectors for TDPAC Measurements.
- TDPAC Study of Group-IVB Metal Oxides in Bulk and Wien2K Calculation.
- TDPAC Study of Group-IVB Metal Oxides in Low Dimension.
- Summary and Outlook.

Chapter 1: Introduction

A general introduction has been furnished in three parts. First part contains the possible details of Group-IVB metal oxides. A little history about the Group-IVB elements, viz., Ti, Zr and Hf, along with some of their relevant properties has been given in a concise form. Then the crystal structures of these three oxides have been described in moderate details as the knowledge of their crystal structure is required to carry out their structural variation including phase transitions.

The second part contains the details about the PAC technique. The historical background of PAC has been given followed by a little theory on the electric quadrupole moment and electric field gradient. Then the theory of directional correlation function has been described. After discussing the unperturbed directional correlation function, the influence of extranuclear fields on the angular correlation function has been introduced. Semiclassically, the interaction produces a precessional motion of the intermediate spin about the symmetry axis defined by the direction of emission of the first γ -ray. Thus the orientation of the intermediate spin gets altered in the time interval between the emission of γ_1 and γ_2 and the angular correlation function is perturbed. Quantum mechanically, the interaction produces the transition among the non-degenerate m-states leading to the emission of γ_2 from an m-state with an attenuated population density. The influence of static electric and magnetic field has been discussed. Then the time-dependent EFG has been introduced. Due to jump diffusion of vacancies in the solids, the tumbling motion of a molecule in a liquid and atomic collision in the gas phase, the magnetic field or electric field gradient arising due to the movement of electric charges, electric or magnetic moments of ions change in a random fashion. The two limiting models, viz., Diffusion Model and Strong Collision Model, explaining the random reorientation of the magnetic field or the EFG at the nucleus have been discussed. The influence of the mode of radioactive decay by the parent atom

to produce the daughter element, viz., electron capture (EC), internal conversion (IC), α - and β -decay, on the directional correlation of γ - γ cascade has been discussed. The methodology of the technique and the different types of PAC techniques has also been presented. The suitability of TDPAC probe and the properties of typical TDPAC probes have been furnished. Lastly, the application of TDPAC technique in the field of solid state physics and chemistry, solid state physics and biology, solution chemistry, super-viscous medium, hot atom chemistry and radiation damage study has been discussed in moderate details.

The last part contains the preliminary aspects of other characterization techniques, viz., X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) etc. The last chapter ends with a concise motivation of the present thesis.

Chapter 2: Development of Fast-Slow Coincidence Setup with LaBr₃(Ce) Detectors for TDPAC Measurements.

This is devoted to the development of a Fast-Slow Coincidence setup for TDPAC measurements used in the present work. The coincidence circuit consists of three planar LaBr₃(Ce) detectors coupled with XP2020URQ Photo Multiplier Tubes (PMTs) having both anode and dynode outputs. The dynode output is used for energy coincidence while the anode output is used for time coincidence. The LaBr₃(Ce) detectors have a better energy resolution than any other scintillation detectors till date and desirable time resolution. The coincidence circuit has a time resolution of 340 ± 10 ps for the 511-511 cascade. The characteristics of the LaBr₃(Ce) detectors with respect to energy linearity and time resolution have also been discussed. The coincidence setup is based on CAMAC data acquisition system where the data are collected in LIST mode so

that the gates in the relevant cascade γ -energies can be applied in the post-acquisition period to extract the coincidence information.

The confidence of the TDPAC data analysis and the scope of application of this technique significantly depend on the time resolution of the coincidence setup. Theoretically the best time resolution means the time response with a delta function. In practice, there exists a finite width in the time response function. This arises due to the detector, photomultiplier tube and the associated electronics. The response function has a Gaussian distribution over the theoretical function. The effect of these electronic modules along with the detectors on the time resolution of the coincidence circuit has been discussed.

Chapter 3: TDPAC Study of Group-IVB Metal Oxides in Bulk and Wien2k Calculation.

The chapter encompasses the experimental details along with the results and discussion of all the studies carried out by TDPAC technique have been presented for Group-IVB oxides in bulk dimension. The anatase and rutile TiO_2 , HfO_2 and ZrO_2 were doped with the TDPAC probe $^{181}\text{Hf}/^{181}\text{Ta}$ by soft chemical co-precipitation method. Then they were counted on the TDPAC spectrometer. Another probe $^{111}\text{In}/^{111}\text{Cd}$ has also been used to look into the occupation of ^{111}In probe-atom at the metal lattice site in the Ti, Zr and Hf oxides and also look into the difference in behavior, if any, for the present PAC probe $^{111}\text{In}/^{111}\text{Cd}$ from our previous probe $^{181}\text{Hf}/^{181}\text{Ta}$. The effect of EC decay in case of $^{111}\text{In}/^{111}\text{Cd}$ probe on the directional correlation pattern has also been studied.

The effect of Mn and Zr-doping on the rutile structure has been performed with TDPAC technique in order to study the metal-metal interaction in doped rutile structure. TDPAC study of 5% Mn-doped TiO_2 indicates that there is no structural change in the TiO_2 matrix due to doping. In another study, the rutile matrix was doped with three different percentage of Zr, viz., 1%, 5%

and 10%. Upto 10% Zr-doping, there is no such significant change in the crystal structure of rutile. The TDPAC parameters remain almost unchanged except an increase in the width of the frequency distribution.

In other experiment, the study of radiation damage on the anatase and rutile crystal structure has also been carried out by following the leaching behaviour of the ^{181}Hf activity from those matrices as well as by the hyperfine study using TDPAC. After incorporating ^{181}Hf tracer into TiO_2 matrix, the leaching property of the resulting matrix was studied in water, sodium chloride and humic acid solutions. The leaching was measured in each of the case by following the radioactivity of ^{181}Hf . TiO_2 matrices were exposed to γ -radiation using ^{60}Co γ -irradiator at a dose of $\sim 5.3\text{kGy/h}$ for 7 days. Then the leaching behaviour was again followed under similar condition and was found to get unaffected by the irradiation. The structural aspects before and after γ -irradiation have been investigated with TDPAC technique which showed that the lattice structure of titania remains undisturbed even under a strong radiation field.

Lastly, the thermal behavior of hafnium oxide fiber has been investigated with the aid of TDPAC technique along with XRD and SEM measurements. This study has yielded a good thermal stability of the fibrous material up to 1173K and the fiber loses its crystallinity to a meager extent at 1673K. No phase transition has been observed up to 1673K in fiber. TDPAC parameters for the HfO_2 fiber annealed at 1173K have been found to be $\omega_Q=124.6$ (3) Mrad/s and $\eta=0.36$ (1). These values remain unaltered for the HfO_2 fiber annealed even at 1673K. Electronic structure calculations based on density functional theory for HfO_2 doped with tantalum has been performed using Wien2K code and calculated EFG parameters are in reasonable agreement with the experimental values.

Chapter 4: TDPAC Study of Group-IVB Metal Oxides in Low Dimension

The chapter focuses the study of Group-IVB oxides in lower dimensions, viz., in thin film of nano dimensions and nanoparticles. The phase transition from anatase to rutile for the 70nm TiO₂ crystallite has been investigated. The study involved the annealing of the TiO₂ nano crystals, adsorbed with the nuclear probe (¹⁸¹Hf/¹⁸¹Ta) at trace level, at different temperatures for different durations. The TDPAC measurement was supported with XRD measurement where the width of the peak increases with the increase in annealing temperature indicating a crystal growth. The samples annealed up to 823K for 4h showed no phase transition, except the growth of the crystallites. However, it showed phase transition at the same temperature (823K), when annealed for longer duration indicating the slower kinetics of the phase transition process. Further the sample, when annealed at 1123K for 4h, showed the phase transition. It has also been observed that the ¹⁸¹Hf tracer, adsorbed on 70nm anatase TiO₂, diffuses from surface to bulk during the phase transition process and the extent of diffusion in anatase differs from that in rutile phase. However, surface to bulk mass-transfer is found to play a significant role in the phase transition process.

The thermal behavior of the TiO₂ shell in the core-shell Ag@TiO₂ system has been investigated by the TDPAC technique in the temperature range from 473K-1073K. These results are supplemented with the TEM and XRD measurements. Although the thickness of the TiO₂ shell increases on annealing as evident from the XRD measurement, the TDPAC results show that the anatase phase persists till 1073K. This is in contrast with the results for the pure TiO₂ nanoparticles of the similar dimensions. These observations suggest that the phase transformation from anatase to rutile is hindered in case of core-shell nanoparticles possibly

because the growth of the shell thickness in case of Ag@TiO₂ nanoparticles is not effective for rutile formation due to the presence of Ag-core.

The structural evolution of Hf metal thin film on Si (111) surface with temperature has been investigated under 10 mbar oxygen pressure. The evolution was characterized by TDPAC technique along with Atomic Force Microscopy (AFM). The Hf-thin film of ~50 nm thickness, deposited on Si (111) substrate by ion-beam sputtering method, was annealed at 673K, 873K and 1073K for 4h. Up to 1073K, there was no signature of monoclinic phase. After annealing at 1273K for 4h, monoclinic phase started to appear along with another component and after 12h at the same temperature, there exists only the monoclinic phase. The thin film was also directly annealed at 1273K for 4h, 8h and 12h. Although after 12h, only the monoclinic phase exists, there was a slight difference in the evolution process. The Hf-silicide formation could not be found by this hyperfine technique under the present experimental condition.

Chapter 5: Summary and Outlook

The present thesis describes the details of a fast-slow coincidence setup with the latest LaBr₃(Ce) detectors, the study of these detectors with respect to energy linearity and time resolution and the versatile application of TDPAC technique in different types of physico-chemical problems. The energy linearity of the detectors could be decided over a range of PM tube bias voltages. The time resolution of the setup was also monitored for different bias voltages. An optimum operational condition could be found from the present work where the energy linearity is maintained without hampering the time resolution of the setup. The coincidence setup was then used for the subsequent TDPAC measurements. At first, the setup was used for the measurement of known TDPAC parameters in case of rutile TiO₂ and it was found that the values exactly match with that mentioned in the literature. After that, the parameters for anatase TiO₂ was found

for the first time with the same PAC setup. The study also confirmed the TDPAC parameters for bulk HfO_2 and ZrO_2 for which the literature data have wide variations. The present thesis also describes for the first time how the PAC technique can be applied to detect the minute difference in metal-metal interactions for doped oxides. It can be perceived from the study that such a small difference in interaction is hard to detect by any other technique. Similarly, the study reveals a small loss of crystallinity and no phase transition at high temperature in case of HfO_2 fiber. The stability of the TiO_2 matrix under strong gamma-field was reviewed by the present hyperfine tool. The technique was also applied in nano dimension of the materials. The theoretical calculation by the Wien2k code based on DFT provides a valuable support to the experimental results. The calculation revealed the information about the electrons of the probe atom Ta contributing to the EFG as well as the charge state of the Ta atom in the fiber matrix. The transfer of the PAC probe from surface to bulk during anatase to rutile phase transition could be identified by TDPAC and such a mass transfer is hardly perceived by any other technique. The present study also describes a comparative study on the stability of anatase phase in case of pure TiO_2 and Ag@TiO_2 core-shell nanoparticles as investigated by TDPAC technique. The surface study in case of evolution of HfO_2 on Si(111) surface has also been described in the present thesis. The present thesis can be summarized in the following way:

- The new $\text{LaBr}_3(\text{Ce})$ -based TDPAC spectrometer coupled to CAMAC data-acquisition system has got unique advantage in its LIST-mode data collection facility.
- The versatile application of TDPAC technique has been presented in the field of different chemical phenomena as well as different dimensions of material ranging from bulk materials in doped form to core-shell nanomaterials.

- The theoretical calculation in combination with experimental results can provide complete information about the electronic environment surrounding the probe atom in atomic scale resolution.

The following studies can be carried out in future:

The present coincidence setup can be modified by coupling the $\text{LaBr}_3(\text{Ce})$ detectors to other fast PM Tubes in order to get a better energy linearity and time resolution. The study of the doped system to identify the metal-metal interaction can be pursued for a number of other doped oxides. Specially, the oxides doped with transition metal are also of practical importance. The study on the radiation stability of the TiO_2 matrix can be further extended by simulating the radiation environment of a high-level nuclear waste and monitoring the similar radiation stability. The similar study can be extended to different nuclear materials and the behavior of those materials under simulated nuclear environment can be studied in minute details. The study with the thin films and nano materials including core-shell type are of real challenge in the field of TDPAC. The similar study with nano-alloys can also be performed with this hyperfine tool.

Publications:

A. Journal:

a. Published:

1. **D. Banerjee**, S.K. Das, S.V. Thakare, P.Y. Nabhiraj, R. Menon, R.K. Bhandari, K. Krishnan; Study of surface-bulk mass transport and phase transformation in nano- TiO_2 using hyperfine interaction technique, *J. Phys. Chem. Solids* 71 (2010) 983–987.
2. **D. Banerjee**, S. K. Das, P. Das, S. V. Thakare, T. Butz; Zr-doped rutile TiO_2 : a nuclear quadrupole interaction study, *Hyperfine Interaction* 197 (2011) 193–198.

3. **D. Banerjee**, R. Guin, S. K. Das, S. V. Thakare; Effect of γ -dose on the crystal structure and leaching behaviour of TiO₂ matrix labeled with ¹⁸¹Hf/¹⁸¹Ta tracer, *J. Radioanal. Nucl. Chem.* 290 (2011) 119–121.
4. **D. Banerjee**, P. Das, R. Guin, S. K. Das; Nuclear quadrupole interaction at ¹⁸¹Ta in hafnium dioxide fiber: Time differential perturbed angular correlation measurements and ab initio calculations, *J. Phys. Chem. Solids* 73 (2012) 1090-1094.

b. **Accepted:**

D. Banerjee and S. K. Das; Study of the Role of Metal Core on the Thermal Behavior of Ag@TiO₂ Core-Shell Nanoparticles, *J. Radioanal. Nucl. Chem.* (In Press).

c. **Communicated:**

1. **D. Banerjee**, S.K. Das, S. V. Thakare, P.Y. Nabhiraj, R. Menon; Nano-phase Evolution of HfO₂ Thin Film on Si (111) Surface: A Nuclear Quadrupole Interaction Study, *Thin Solid Films*.

B. Other Publications:

1. **D. Banerjee**, R. Guin & S.K. Das; Study Of Leaching Property of TiO₂ matrix labeled with ¹⁸¹Hf, *Nuclear and Radiochemistry Symposium (NUCAR)-2009*.
2. **D. Banerjee** and S. K. Das; Annealing Behavior of Hafnium Oxide Fiber Used as a Target for Radioactive Ion Beam Preparation, *Synthesis and Characterization of Smart Materials-2009*.
3. **D. Banerjee**, P. Ghosh, R.K. Chatterjee and S. K. Das; Hyperfine interaction study of 5% Mn⁺² doped TiO₂, *Condensed Matter Days-2009*.
4. P. Das, **D. Banerjee** and S. K. Das; Electronic and structural properties of anatase and rutile TiO₂ doped with Ta: Experimental study and *ab initio* calculations, *Joint International Conference on HFI and NQI-2010*.

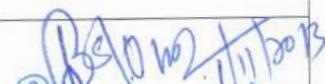
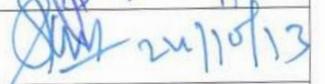
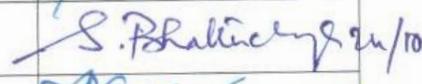
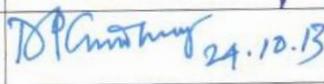
5. **D. Banerjee** and S. K. Das; Nano-phase Hindered Evolution of HfO_2 Thin Film on Si (111) Surface: A Nuclear Quadrupole Interaction Study, *Joint International Conference on HFI and NQI-2012*.
6. **D. Banerjee**, P. Das, S.V. Thakare and S.K. Das; Study of Annealing Behavior of Probe Lattice Interaction in Gr-IVB oxides by Nuclear Quadrupole Interaction, *NUCAR-2013*.
7. **D. Banerjee**, S. Bhattacharya, T. Bhattacharjee and S.K. Das; Fast-slow coincidence measurements with $\text{LaBr}_3(\text{Ce})$ detectors, *NUCAR-2013*.



Date: 22.10.2013

(Signature of Student)

Doctoral Committee:

S. No.	Name	Designation	Signature with Date
1	Prof. B. S. Tomar	Chairman	 24/10/13
2.	Prof. S. K. Das	Convener	 24/10/13
3.	Prof. S. Bhattacharya	Member	 24/10
4.	Dr. D. P. Chowdhury	Member	 24.10.13