Chapter 5. Summary and Outlook

This thesis describes the potential of the γ-γ Perturbed Angular Correlation Technique applied to both the bulk and lower dimension of materials. The application of this technique in the nanomaterials including core-shell nanoparticles and thin films is very limited. The method of labeling the samples with the nuclear probe has been carried out under mild condition and with ~ 0.1atom% concentration of the probe so that the material property of the host matrix does not get affected. The TDPAC spectrometer is based on CAMAC electronics where the data are collected in LIST mode. The setup has got $LaBr_3$(Ce) detectors coupled with fast PM Tubes. The optimum operational condition has also been determined by the characteristics study of these detectors under different working conditions. The time resolution of the system has been determined with the new setup.

The characteristics of the new $LaBr_3$(Ce) detectors have been studied at different bias voltages of the PM Tube. The linearity of the energy response for these detectors has been followed with varying bias voltages. The dependence of the time resolution of the coincidence setup with the PM Tube bias has been looked into in order to determine the optimum working condition of this coincidence setup based on the $LaBr_3$(Ce) detectors. The TDPAC parameters for the bulk TiO_2, ZrO_2 and HfO_2 have been determined following the present method of sample preparation based on coprecipitation technique. In this case two probes, viz., ^{181}Hf/^{181}Ta and ^{111}In/^{111}Cd, have been used. First probe was produced by neutron irradiation method while the second probe was obtained by charged particle reaction at VECC, Kolkata. The high cross-section of ^{180}Hf (natural abundance~35%) for thermal neutron absorption (~13barn) produces sufficient amount of the probe ^{181}Hf/^{181}Ta which is subsequently used along with the other Hf-isotopes. On the other hand, the ^{111}In-probe, after its production, is separated in carrier-free form and then used for

subsequent study. The strength of EFG is comparable in case of rutile TiO_2, HfO_2 and ZrO_2 for both the probes. However, the strength of EFG is lower in case of anatase TiO_2. This observation is expected from the corresponding crystal structures of the oxides. The rutile matrix has been doped with one transition element Mn and another same group element Zr. The effect of the doping has been investigated with the TDPAC method. The $^{181}Hf/^{181}Ta$ was used as the PAC probe in the present study. The interaction of the probe atom with the dopant atom is different from that with the host atoms. This is not reflected in the mean values of the interaction frequency and the asymmetry parameter. The width of the frequency distribution has been found to increase steadily with the dopant concentration. So the hyperfine technique TDPAC can be utilized to investigate the role of dopant in the host matrix and its interaction with the host atoms. The effect of varying concentration of dopant can also be looked into by this microscopic tool.

The radiation-damage study of the rutile matrix has been carried out with TDPAC technique. For this, the leaching of Hf from TiO_2 matrix has been investigated in different media, like, water, NaCl solution and humic acid solution. The selection of the leaching media stems from the fact that water is the most common medium of contact, NaCl solution simulates the medium of sea-water and humic acid solution represents the soil environment.In all the cases, the leaching has been monitored by following the radioactivity of ^{181}Hf tracer. The effect of γ-dose on the crystal structure of TiO_2 has been investigated with the hyperfine interaction technique, viz., TDPAC and it has been correlated with the leaching behavior of TiO_2. The TiO_2 matrix has so stable crystal structure that it is not disturbed by a long γ-irradiation and Hf, simulant for actinide in high-level waste, is strongly adhered in the TiO_2 matrix which might thus be used as an immobilizing medium for nuclear waste.

A hyperfine interaction study of the process of phase transition in nano TiO_2 from anatase to rutile phase has been carried out. The phase transition in 70nm TiO_2 could be described in the following way. The surfaces of the nano particles roll over each other during the annealing process causing the growth in the crystallite and the $^{181}Hf/^{181}Ta$ probe from the surface gets transferred into the bulk which transforms into the rutile phase and partly remains as anatase. The probe gets into the rutile phase either during the process of phase transition or due to diffusion after the rutile is formed or both. The phase transition incorporates a temperature-mediated mass transfer from surface to its bulk.

The same technique has been used to elucidate the thermal behavior of $Ag@TiO_2$ core-shell nanoparticles and compare the similar behavior for pure TiO_2 nanoparticles. The anatase to rutile phase transformation does not follow the same trend in the two systems. In case of core-shell nanoparticles, even after attaining the critical size for rutile phase transformation at 1073K, rutile structure could not be attained. But, for pure TiO_2 nanoparticles, the rutile phase starts to appear at 1073K and at a grain size of 16nm. This core-shell structure thus modifies the nature of phase transition as well as its rate either due to a chemical interaction between metal core and semiconductor shell or due to an insufficient effective grain growth of TiO_2 shell in case of $Ag@TiO_2$nanoparticles.

The formation of monoclinic phase of HfO_2 from the metallic Hf deposited on Si (111) surface under 10mbar O_2 pressure has been studied using TDPAC. The change in the morphology of the surface of the ~50 nm thin film with the annealing process has also been followed by AFM measurements and correlated with the PAC results. The amorphous HfO_2 phase associated with large amount of defects is formed from the metallic Hf and remains amorphous upto 1073K. However, when it is annealed at 1273K the monoclinic phase starts to appear along with 3D-

island formation and the percentage of monoclinic phase increases with the duration of annealing at the same temperature. Hence the kinetics of this evolution process is slow. It is only the monoclinic HfO_2 phase which exists after annealing at1273K for 12h. Non-existence of any other component in the TDPAC spectrum rules out the formation of any Hf-silicide phase in the present work.

The fibrous HfO_2, used as the RIB target material, doped with $^{181}Hf/^{181}Ta$ probe was studied using the TDPAC technique where ^{181}Ta occupying the Hf sites acted as a TDPAC probe. HfO_2 fibrous samples were annealed at different temperatures in 1000-2000K range and the structural aspects were investigated in the samples annealed at such high temperatures using TDPAC technique.

In order to understand the TDPAC results obtained from the ^{181}Ta doped HfO_2 fibrous sample and also the annealing effects on these samples, the first principle electronic structure calculations were performed based on density functional theory (DFT) using WIEN2K code. DFT calculation of the HfO_2 system indicates that the ^{181}Ta probe is in the charged state in the lattice position and the contribution of the EFG is mainly due to the p-electrons. Density of states indicates that the doping with Ta does not affect the neighboring Hf atoms of the host. As a result, EFG parameters of the fiber having 6-7 μm diameter doped with Ta are expected to remain unaltered compared to those of bulk HfO_2.