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# Nuclear quadrupole interaction at $^{181}$Ta in hafnium dioxide fiber: Time differential perturbed angular correlation measurements and ab initio calculations

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ABSTRACT

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



## 1. Introduction

A suitable refractory material which can be heated to elevated temperatures is an essential requirement for an efficient production of the radioactive ion beams (RIB) using the isotope separation on-line (ISOL) technique [1]. At a high temperature, there is a fast release of the product species from the target but at the same time there should not be sufficient vaporization or sublimation of the target material itself. Among various refractory materials viz. $HfO_2$, $Y_2O_3$, $CeO_2$, $Al_2O_3$ etc. satisfying the physical, chemical, metallurgical and thermodynamical properties, hafnium oxide ($HfO_2$) has been considered as a potential RIB target material [1]. The temperature at which the vapor pressure of the target material reaches $10^{-4}$ Torr is the highest (2773 K) for $HfO_2$. Moreover, Hafnium being the highest $Z$ element among the metal ions of the above mentioned materials, the stopping range of the recoil products is the least in $HfO_2$ and thus the reaction products cannot penetrate deep below the surface and would be released faster thereby increasing the efficiency of the RIB intensity. Fibrous targets of $HfO_2$ have been used successfully for the production of the $^{17}$F radioactive beam [2]. It has been observed that the $HfO_2$ targets can be operated at higher temperatures (2373–2573 K) compared to the others leading to a more efficient release of the required radioactive isotopes [3]. The properties of the targets using $HfO_2$ in various forms are studied for the RIB facility which is being developed at Variable Energy Cyclotron Centre (VECC), Kolkata, incorporating the traditional ISOL technique [4]. According to the simulation studies, it is found that the temperature at the $Al_2O_3$ target would be 1000–2000 K depending on the energy deposited by the proton or alpha beam used for the irradiation. It is expected that the $HfO_2$ fibrous targets for the RIB production would be heated to such high temperatures under similar irradiation conditions. In addition, $HfO_2$ has several other applications [5,6] due to its high mechanical hardness, significant thermal stability and high refractive index. $HfO_2$ having a high dielectric constant can be considered as a gate dielectric in the form of thin film [7,8]. A recent study [9] describes the annealing behavior of the $HfO_2$ thin film. Since with the temperature $HfO_2$ undergoes a polymorphic structural transition [10] from monoclinic (RT-1443 K) to tetragonal (1443–2643 K) to cubic ( $>$2645 K), it is imperative to study the structural transformation of fibrous $HfO_2$ in this temperature range.

In this present work we studied the fibrous $HfO_2$ doped with $^{181}$Hf/$^{181}$Ta probe using the time differential perturbed angular correlation (TDPAC) technique where $^{181}$Ta occupying the Hf sites acted as a TDPAC probe. We annealed $HfO_2$ fibrous samples at different temperatures in 1000–2000 K range and investigated the structural aspects in the samples annealed at such high temperatures using TDPAC technique. Due to the fact that the available data on bulk $HfO_2$ having monoclinic structure [11,12] with the unit cell dimensions as $a$=5.1156 (5) Å, $b$=5.1722 (5) Å and $c$=5.2948 (5) Å shows a wide variation in the measured

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quadrupole frequency [13–16], we also experimentally determined the TDPAC parameters for the bulk $HfO_2$ samples prepared by the precipitation of hafnium hydroxide labeled with $^{181}$Hf tracer followed by heating it at 1173 K for 6 h. With a comparative study with the bulk sample, TDPAC data would also indicate any structural change that may have occurred while the fibers of $HfO_2$ are formed or during the annealing process.

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, we performed the first principle electronic structure calculations based on density functional theory (DFT) [17] using WIEN2K code [18]. We first studied the electronic structures of the bulk $HfO_2$ as we expect that understanding the electronic distribution around the probe $^{181}$Ta and sources contributing to the electric field gradient (EFG) at the probe site in a bulk sample would lead to a better understanding of the changes that would occur when a fiber or the thin film of $HfO_2$ is prepared and annealed thereafter.

## 2. Experimental

### 2.1. Sample preparation

The $HfO_2$ fiber (make: Zicar Zirconia Inc., USA; purity: 99 wt%) of diameter 6–7 μm and density 1.21 g/cm$^3$ was used in the present experiment. $^{181}$Hf tracer was produced by $^{180}$Hf$(n,\gamma)^{181}$Hf irradiating $HfO_2$ fiber in a thermal neutron flux of $1.0\times10^{13}$ neutrons per cm$^2$ per second in DHRUVA reactor at Bhabha Atomic Research Centre, Mumbai, India. A part of the irradiated sample was annealed at 1173 K for 6 h and the other part at 1673 K for 6 h. Then both the samples were counted for TDPAC at room temperature. The inactive counterparts of the sample, annealed under identical conditions, were used for the XRD and SEM measurements. Bulk $HfO_2$ was prepared by precipitating hafnium hydroxide $Hf(OH)_4$ from $HfCl_4$ solution by adding ammonia solution in presence of $^{181}$Hf tracer. This precipitate was centrifuged, dried and heated at 1173 K for 6 h. This sample was then counted on the TDPAC setup mentioned below.

### 2.2. TDPAC measurement

Four samples viz. unannealed, annealed at 1173 K and 1673 K and the bulk $HfO_2$ were counted with the fast–slow coincidence of 133–482 keV cascade of the probe $^{181}$Ta using a coincidence system consisting of three $BaF_2$ detectors. The coincidence data acquisition was performed in the LIST mode with the help of a CAMAC electronics mentioned elsewhere [19]. Individual time spectra at 90° and 180° angles were obtained by applying the cascade energy gates through software in the post-acquisition period. The time resolution of the setup was 0.9 ns (FWHM) in the 133–482 KeV cascade gate.

The Nuclear Quadrupole Interaction (NQI) of the $I=5/2$ intermediate state leads to a splitting in three substates with $m=\pm1/2$, $\pm3/2, \pm5/2$. The perturbation function is given by [20]

$$G_2(t)=a_0+a_1\cos\omega_1 t+a_2\cos\omega_2 t+a_3\cos\omega_3 t$$

with the transition frequencies among these levels are $\omega_1$, $\omega_2$ and $\omega_3$ which can be expressed in terms of the quadrupole frequency.

$$\omega_Q=\frac{eQV_{zz}}{40\hbar}$$

with $Q$ denoting the quadrupole moment of the intermediate state and $V_{zz}$ being the largest component of the field gradient tensor.

The experimental data were fitted with this function modified using a finite distribution of $\omega_Q$. In the present case we have used the Lorentzian distribution. The final form of the theoretical function in which the experimental data were fitted is given by

$$G_2(t)=a_0+\sum_{n=1}^{3}a_n\exp(-\omega_n\delta t)\times\exp(-1/2\omega_n^2\tau^2)\cos(\omega_n t)$$

The exponential damping terms attribute to the finite resolving time characterized by a Gaussian distribution with a standard deviation $\tau$ and the Lorentzian frequency distribution relative to width parameter $\delta$. The coefficients $a_n$ have dependence on the nuclear radiation parameters and the asymmetry parameter $\eta=(V_{xx}-V_{yy})/V_{zz}$.

## 3. Theoretical calculation

Ab-initio study of the Ta-doped $HfO_2$ bulk samples has recently been done [21] where the effect on EFG parameters around the probe atom due to the charge state considerations has been observed but it has not been elucidated. In the present work, we have performed the electronic structure calculations based on the density functional theory (DFT) and used the augmented plane wave plus local orbital (APW+LO) method as embodied in the WIEN2K code [18] in order to understand the effect of charge state on the EFG parameters. The exchange and correlation effects were included in our calculation using Generalized Gradient Approximation (GGA) [22]. The basic input requirement for these electronic structure calculations of a crystal are the cell settings and lattice parameters. These required structure parameters used in our calculations are the same as mentioned earlier. The crystal structure of $HfO_2$ is monoclinic where there are four $HfO_2$ molecules in each unit cell and each Hf metal ion is surrounded by seven oxygen atoms. Since the doping of $HfO_2$ samples with $^{181}$Ta probes for the TDPAC studies were produced by irradiating the $HfO_2$ samples with thermal neutrons, the recoil of the probe nucleus is negligible. However, the recoil due to the prompt gamma emission cannot be neglected. Though there is an evidence of recoil induced damage [9], it is expected that these will be removed when the sample is annealed at high temperatures in the present experiment. As we know that the electric field gradient which determines the hyperfine parameters is extremely sensitive to the electronic environment around the probe site, the charge state of the probe atom is of prime consideration. In order to decide whether Ta would remain in 5+ state at the probe site as it would exist in a pure tantalum compound or there would be a change in the charge state of the probe Ta atom, we performed two independent calculations. In one case we assumed no change in the charge state of the dopant Ta atom as it replaced Hf atom and called it as neutral state calculations. We found partially filled impurity levels having Ta "*d*" and oxygen "*p*" character. In the second case referred to as the charge state calculation, we assumed that tantalum would act as a donor impurity. So, we removed one valence electron from the unit cell, neutralized the charge by adding one electron to the homogeneous negative background and thereafter performed the self-consistent calculations. It is interesting to note that the variation in EFG parameter around the probe atom Ta considering the neutral and charge state configurations is in agreement with the earlier work [21]. There is a speculation that Ta exists in two different charge states in Ta-doped monoclinic $HfO_2$ and considerable amount of the magnetic moment can be induced depending on impurity charge state [23]. We determined the $V_{zz}$ component of EFG for different *l*-projected states and studied the contribution to EFG at Ta site from the electrons having different *l*-values.