

## TDPAC studies of Hf doped YBCO

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**Abstract.** Time differential perturbed angular correlation measurements of the 133–482 keV  $\gamma$ - $\gamma$  cascade of  $^{181}\text{Ta}$  in Hf-doped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  are presented. The  $^{181}\text{Hf}$  precursor nuclei are incorporated into the sample by thermal neutron irradiation. Two quadrupole interaction frequencies are observed in the as-irradiated sample:  $\nu_{Q1} = 161 \pm 10$  MHz with intensity  $f_1 = 75\%$ , asymmetry parameter  $\eta_1 = 0.32$  and damping parameter  $\Lambda_1 = 0.42$ , and  $\nu_{Q2} = 1108 \pm 40$  MHz with  $f_2 = 25\%$ ,  $\eta_2 = 0.62$ , and  $\Lambda_2 = 0.60$ . On annealing the sample in air at various temperatures  $T_a$  and quenching to room temperature,  $f_1$  remained nearly constant for  $T_a < 600^\circ\text{C}$  and  $\nu_{Q1}$  for all annealing temperatures indicating that these are insensitive to oxygen stoichiometry. This frequency is interpreted to be due to  $^{181}\text{Hf}$  substituting Y sites. Beyond  $T_a = 600^\circ\text{C}$ ,  $f_1$  increased and reached a constant value of 90% for  $T_a = 800^\circ\text{C}$ . The value of  $\nu_{Q2}$  showed a slight variation between 1086 and 1160 MHz, while  $f_2$  remained nearly constant at 25% for  $T_a < 600^\circ\text{C}$ . This component is identified to be due to  $^{181}\text{Hf}$  substituting Cu 1 sites in the Cu–O chains of YBCO. Above  $600^\circ\text{C}$   $\nu_{Q2}$  decreased and reached a value of 808 MHz beyond  $750^\circ\text{C}$ .

**Keywords.** Perturbed angular correlation; quadrupole interaction; Hf-doped YBCO; high  $T_c$  superconductor.

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### 1. Introduction

A detailed knowledge of the electronic and structural properties of the high temperature oxide superconductors is crucial for understanding their superconducting properties. Studies on doped  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$  with the dopants substituting for Y, Ba or Cu site have proved very useful in understanding the superconducting properties of the system [1]. Information about the local structure, nature of defects and their ordering may be obtained by use of nuclear probes [2–5]. Information on the local structure and symmetry can be obtained from a knowledge of the electromagnetic fields at the site. The fact that the electromagnetic fields at a lattice site in a matrix sensitively depend on the nature of the electron density distribution in the neighbouring sites and the local symmetry, has led to a considerable amount of work using hyperfine interaction techniques like muon spin rotation spectroscopy ( $\mu\text{SR}$ ), time differential perturbed angular correlation (TDPAC), and Mössbauer Effect (ME) on high temperature superconducting ceramics [6–8]. Atomic jump and relaxation processes in solids can also be studied through time dependent hyperfine interactions [9]. Even though a large amount of work has been done in the oxide superconductors using the PAC probe  $^{111}\text{Cd}$ , the results are not consistent with respect to the magnitudes of the quadrupole coupling constants, their temperature dependence, asymmetry parameters and

intensity ratios [10–13]. The site occupancy of the probe atoms in the above investigations is also not established unambiguously. The disadvantage here is that the most commonly used PAC precursor atoms such as In, Hf and Ru are not among the atomic constituents of the ceramic superconductors. Further even in single phase material the occupancy site of the PAC probe is uncertain owing to the existence of different cation sites. Hence the effort is still on for the determination of the correct location of these probes in YBCO samples. These oxide based superconductors are very sensitive to humidity which would cause the deterioration of the sample and thereby change the hyperfine interaction parameters [13]. Hf doping into YBCO increases the resistance to deterioration by aging and humidity significantly [14]. Hence TDPAC measurements could be done over a period of time keeping the sample less susceptible to humidity and oxygen stoichiometry variations. The present work involves introducing Hf, a 5d transition element, into YBCO, characterizing the sample by a variety of techniques, neutron activation of the sample to produce  $^{181}\text{Hf}$  and determining the local structure around the probe nucleus by measurement of  $^{181}\text{Ta}$  TDPAC. Even though Akselrod *et al* [15] have reported preliminary measurements of TDPAC using  $^{181}\text{Hf}$ , these have not been made as a function of oxygen stoichiometry. The present work is aimed at determining the hyperfine interaction parameters at various oxygen stoichiometries by subjecting the well characterized Hf-doped YBCO samples to suitable annealing and quenching treatments as part of a programme for a detailed elucidation of the properties of the system. The experimental details are given in §2. The results are presented and discussed in §3. The main conclusions are given in §4.

## 2. Experimental

Samples of Hf doped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  with Hf content of 1.0 at% of Cu [16] were prepared by the standard solid state reaction method [17], starting with appropriate quantities of 99.99% pure  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ ,  $\text{CuO}$  and  $\text{HfO}_2$ . X-ray powder diffraction measurements on the final oxygen-treated sample indicated that it is orthorhombic in structure and the lattice parameters are the same as that of undoped sample. Further characterization of the sample was done prior to irradiation using a CAMECA secondary ion mass spectrometer. It was found that Hf was doped homogeneously in the sample by scanning the depth profiles of Hf as well as each of the other constituents of the sample. The superconducting transition temperature was determined to be  $T_c = 85$  K by AC susceptibility measurements.

The Hf-doped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  sample was irradiated with thermal neutrons in the CIRUS reactor at the Bhabha Atomic Research Centre, Bombay to a fluence of  $2 \times 10^{18}$  n/cm<sup>2</sup> to produce the  $^{181}\text{Hf}$  activity. The temperature of the sample during irradiation was 50°C. Even though the other constituents of the sample are activated during irradiation they decayed in a short period. The  $\gamma$  ray spectrum measured two weeks after irradiation using a high pure Ge detector showed only peaks corresponding to  $^{181}\text{Hf}$  activity in the sample. TDPAC measurements were done on this sample first in the as-irradiated state and then after annealing it at different temperatures and quenching to room temperature. After the decay of the radioactivity the samples were again checked for superconductivity by susceptibility measurement. It was found that the transition temperature was not affected appreciably by the neutron irradiation and due to aging.

The time differential perturbed angular correlation of the 133–482 keV  $\gamma$ – $\gamma$  cascade

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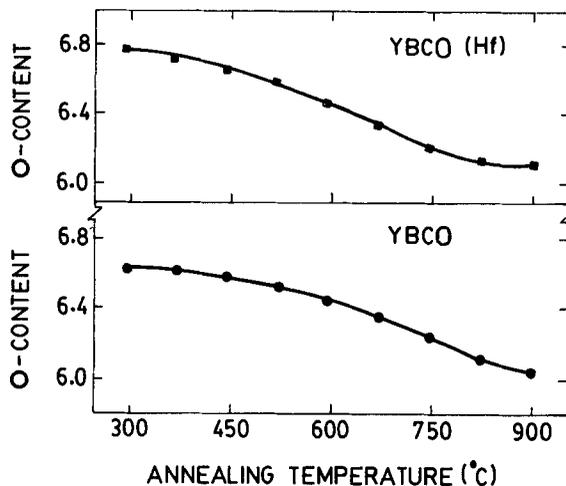
of  $^{181}\text{Ta}$  was measured by a three-detector twin fast-slow coincidence set up [18]. The common movable detector was gated for the START (133 keV)  $\gamma$  ray while the other two detectors fixed at right angles to each other detected the STOP (482 keV)  $\gamma$  ray. The START detector was moved at periodic intervals between  $90^\circ$  and  $180^\circ$  positions with respect to either of the STOP detectors and the delayed time resolution spectra were obtained in the form of count rate as a function of the time elapsed after the emission of the first  $\gamma$  ray. Hence for each position of the START detector two time spectra  $W(90, t)$  and  $W(180, t)$  were recorded simultaneously. The prompt time resolution of the set-up measured with a  $^{60}\text{Co}$  source was 2.2 ns FWHM when gated for the above cascade.

Irradiated samples were heated in air for 30 min at various temperatures from  $100^\circ$  to  $900^\circ\text{C}$  and quenched to room temperature. TDPAC measurements were carried out at room temperature after each annealing treatment. After this set of measurements were done, the sample was subjected to the following heat treatment in oxygen atmosphere. The sample was annealed at  $900^\circ\text{C}$  for 15 h and slow cooled to  $600^\circ\text{C}$  at the rate of  $20^\circ\text{C/h}$ . It was kept at  $600^\circ\text{C}$  for 15 h, and then slow cooled to  $400^\circ\text{C}$ , kept at this temperature for 15 h and subsequently slow cooled to room temperature. The TDPAC measurements were made on this heat treated sample. Oxygen stoichiometry of the sample was inferred from a modified iodometric titration measurement [19] made on representative unirradiated samples from the same lot. After each heat treatment oxygen stoichiometry was determined from the initial value of  $x$  and the weight of the sample. The variation of oxygen stoichiometry with annealing temperature for undoped and Hf-doped YBCO is shown in figure 1.

From the time delayed coincidence spectra  $W(90, t)$  and  $W(180, t)$  the normalized anisotropy function  $R(t)$  was calculated as

$$R(t) = A_{22} G_{22}(t) = 2 \frac{W(180, t) - W(90, t)}{W(180, t) + 2 W(90, t)} \quad (1)$$

where  $G_{22}(t)$  is the perturbation factor and  $W(90, t)$  and  $W(180, t)$  are the coincidence count rates at angles  $90^\circ$  and  $180^\circ$  respectively between the START and STOP



**Figure 1.** Oxygen content vs annealing temperature in undoped and Hf-doped YBCO.

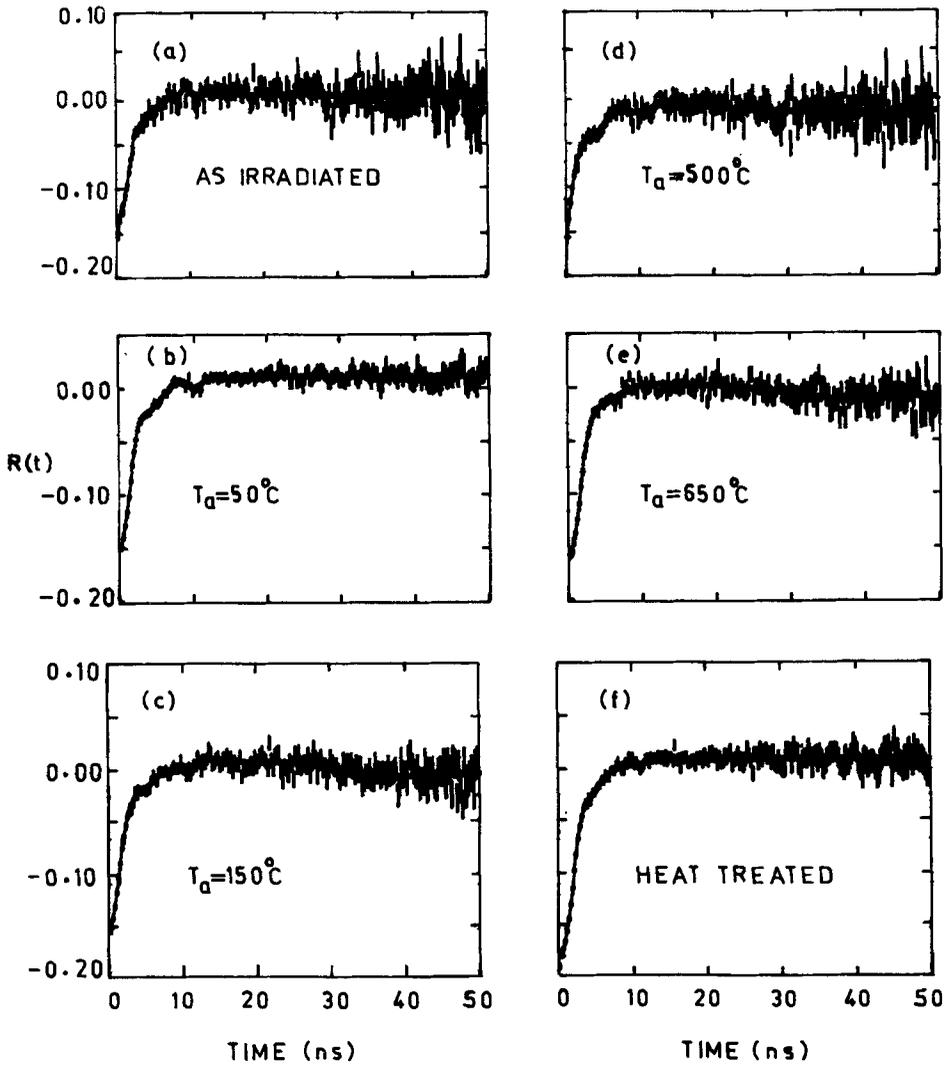


Figure 2. The experimental  $R(t)$  vs  $t$  spectra at room temperature after each annealing treatment: (a) as-irradiated, (b)  $T_a = 50^\circ\text{C}$ , (c)  $T_a = 150^\circ\text{C}$ , (d)  $T_a = 500^\circ\text{C}$ , (e)  $T_a = 650^\circ\text{C}$  and (f) heat treated (see text). The continuous curves are those calculated using the fitted values of parameters.

detectors. The anisotropy function  $R(t)$  was averaged over the two sets corresponding to the two STOP detectors. Typical  $R(t)$  vs time curves for representative heat treated samples are shown in figure 2. The fourier transform of the experimental curves  $R(t)$  indicated the presence of two frequencies. The spectra were least squares fitted to the function [20, 21]

$$R(t) = A_{22} G_{22}(t) = \sum_{i=1}^2 f_i A_{22} G_{22}^i(t) \quad (2)$$

$$A_{22} G_{22}^i(t) = A_{22} S_{20}^i + \sum_{n=1}^3 S_{2n}^i(\eta_i) \cos(\omega_n^i t) \exp(-\delta\omega_n^i t) \quad (3)$$

where  $f_i$  is the relative fraction of nuclei experiencing a quadrupole interaction (QI) frequency  $\omega_n^i$  and  $\sum_{i=1}^3 f_i = 1$ . The amplitudes  $S_{2n}$  were treated as free parameters satisfying the condition  $\sum_{n=0}^3 S_{2n} = 1$ . The factor  $\exp(-\delta\omega_n^i t)$  accounts for the damping of the anisotropy due to a distribution (assumed to be Lorentzian) of quadrupole frequencies, with width  $\delta\omega_n^i$  around the mean values  $\omega_n^i$ . The damping parameter is given by  $\Lambda_i = \delta\omega_n^i/\omega_n^i$ . For  $^{181}\text{Ta}$  the spin of the intermediate level,  $I = 5/2$  for which we get

$$\nu_{Qi} = eQV_{zz}/h = 20\omega_1^i/\pi \quad (4)$$

where  $V_{zz}$  is the principal component of the electric field gradient (EFG) tensor. When the EFG is not axially symmetric, the asymmetry parameter

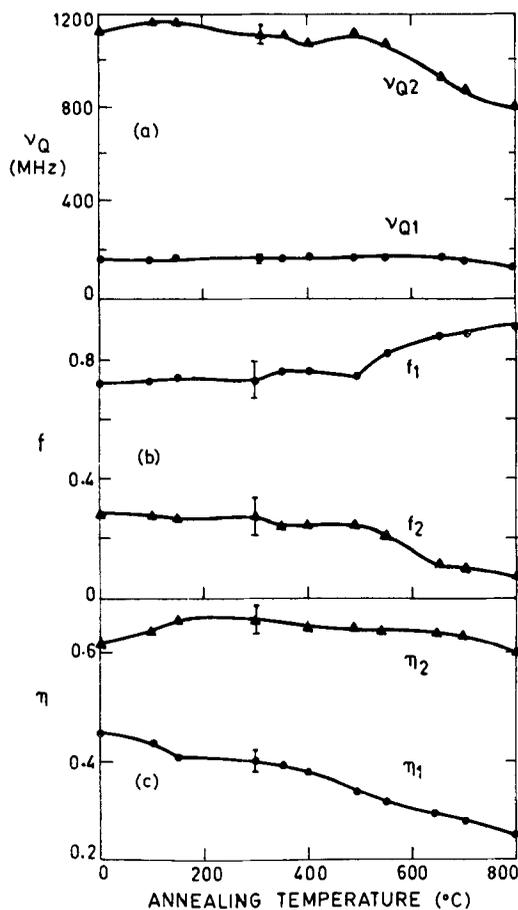
$$\eta = (V_{xx} - V_{yy})/V_{zz}, \text{ where } |V_{zz}| > |V_{yy}| > |V_{xx}| \quad (5)$$

is extracted from the fit of the data to equations 2 and 3.

### 3. Results and discussion

TDPAC spectra of the sample in the as-irradiated condition and after each annealing treatment (figure 2) showed an aperiodic perturbation due to a static quadrupole interaction characterized by a very broad distribution of quadrupole interaction frequencies. The least squares fit of the spectrum in the as-irradiated sample (figure 2) showed that about 75% of probe nuclei experience a quadrupole interaction frequency,  $\nu_{Q1} = 161 \pm 10$  MHz with a damping parameter  $\Lambda_1 = 0.42$  and the remaining nuclei experience a frequency  $\nu_{Q2} = 1108 \pm 40$  MHz with a damping parameter  $\Lambda_2 = 0.60$ . The variation of the quadrupole coupling constants, their intensities and asymmetry parameters with annealing temperature is shown in figure 3. In 1 at% Hf-doped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , the transition from the orthorhombic phase produced by quenching from low temperatures to the tetragonal phase produced by quenching from high temperatures occurs when  $x = 0.6$  corresponding to  $T_a = 650^\circ\text{C}$ . This is less than the  $T_a$  at the transition in undoped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  by about  $25^\circ\text{C}$ . The Hf doping in YBCO results in an increase of oxygen stoichiometry at all annealing temperatures as can be seen in figure 1.

Even though it is not possible to pin point unambiguously the lattice location of Hf in YBCO directly from experiments, the following systematic arguments lead us to interpret that the  $\nu_{Q1}$  is due to Hf substituting Y sites and  $\nu_{Q2}$  due to Hf substituting Cu 1 site in the Cu-O chain. Firstly  $\nu_{Q1}$  frequency and also the fraction (75%) of nuclei experiencing this are invariant with annealing temperature as seen in figure 3. This gives an indirect evidence for the occupation of either Y or Ba site. Secondly a low value of the QI frequency is consistent with the more symmetric nature of the Y site than other sites, especially Ba site. Thirdly since the Y site is far from the Cu-O chains, any substitution in this would only result in a reduction of the effective Cu valence. This can be explained as follows. Substitution of  $\text{Y}^{3+}$  by  $\text{Hf}^{4+}$  leads to the reduction in the charge density at the Y site. Also it results in the increase in the Cu1-O3 interatomic distance, which causes a reduction of the electron deficiency in the complex Cu1-O. This is analogous to the case of Pr substituting Y sites [22]. If  $^{181}\text{Hf}$  nuclei substitute for Ba site it enhances the oxygen stoichiometry, especially in the Cu-O chain region [23] and hence should result in the variation of QI frequency. But it is found from figure 3(a) that for annealing temperatures below  $600^\circ\text{C}$   $\nu_{Q2}$



**Figure 3.** Variation of (a) quadrupole coupling constant, (b) intensity and (c) asymmetry parameter with annealing temperature.

shows only a small change, but shows a larger decrease above 600°C. Substitution in Ba sites would have resulted in an increase in the frequency or no variation at all. Fourthly as the ionic radius of  $\text{Hf}^{4+}$  (0.81 Å) is somewhat less than that of  $\text{Y}^{3+}$  (0.93 Å)  $\text{Hf}^{4+}$  can easily substitute the latter. From figure 3 it can also be seen that the value of  $\eta_1$  decreases with annealing temperature. This can be understood as due to the decrease in orthorhombic distortion with increasing  $x$ . Another important point to be noted is that even at  $x = 1$  ( $T_a = 800^\circ\text{C}$ ),  $\eta_1$  did not reach zero, implying a local orthorhombic structure, consistent with the result reported earlier by others [12]. Although  $f_1$  remained constant at 75% for  $T_a < 600^\circ\text{C}$ , it increased to about 90% between 600°C and 800°C as shown in figure 3. The damping parameter remained nearly constant at 0.42. For  $T_a < 600^\circ\text{C}$   $\nu_{Q2}$  shows a variation from 1086 to 1160 MHz and hence its sensitivity to oxygen stoichiometry (see figure 3). Akselrod *et al* have reported a frequency of  $1086 \pm 45$  MHz in the heat treated Hf-doped YBCO sample. This value is in agreement with  $\nu_{Q2}$  obtained in the present case. Taking into account the ion-O distance and the ionic radii of  $\text{Hf}^{4+}$  and  $\text{Cu}^{2+}$  this is interpreted as due to Hf in Cu1 site in Cu-O chains again in agreement with Akselrod *et al*. However  $\nu_{Q1}$  has not been reported by them. For  $T_a$  between 650°C and 800°C  $\nu_{Q2}$  decreases rapidly reaching a value of 808 MHz at  $T_a = 800^\circ\text{C}$ . The latter value is close to that

due to  $\text{HfO}_2$ . But the fraction of nuclei experiencing this QI is only 10%, the remaining fraction experiencing  $161 \pm 10$  MHz. The  $\nu_{Q2}$  frequency is found to be close to the one obtained for  $^{181}\text{Ta}$  in Hf oxides with oxygen vacancy stabilized cubic phase [24, 22]. This indicates that for  $x > 0.6$  about 10% of the probe nuclei in the sample occupy sites whose oxygen environment is similar to that in the stabilized oxides.

After the above quenching measurements were done, the sample was once again heat treated and thereby taken to orthorhombic phase. TDPAC measurement on this heat treated sample was done. The analysis of this resulted in  $\nu_{Q1} = 162 \pm 10$  MHz and  $\nu_{Q2} = 1084 \pm 40$  MHz. These values are the same within error limits as the starting values in the orthorhombic phase. This shows that the sample has been restored to its original form by heat treatment. This process is repeatable.

Thermal neutron irradiation of the Hf-doped YBCO to fluences attained in the present work ( $2 \times 10^{18}$  n/cm<sup>2</sup>) did not produce any appreciable effect on the defect properties and the superconductivity of the sample. The estimated recoil energy due to  $(n, \gamma)$  reaction in  $^{180}\text{Hf}$  is quite small. Therefore thermal neutron irradiation does not produce appreciable displacement damage in the sample at the temperature of irradiation. Also the recoil energy due to beta decay of  $^{181}\text{Hf}$  to the PAC probe nucleus  $^{181}\text{Ta}$  is only of the order of 1.7 eV. Therefore these two processes do not produce any effect on the sample.

#### 4. Conclusion

The present TDPAC study has shown that when Hf doped YBCO is in the orthorhombic phase about 75% of the probe nuclei substitute for Y sites with an average quadrupole interaction frequency of  $161 \pm 10$  MHz and the remaining for Cu1 sites in Cu-O chains with a quadrupole interaction frequency of  $1108 \pm 40$  MHz. After each annealing and subsequent quenching treatments leading to the sample in the tetragonal phase it is found that 90% of the probe nuclei substitute for Y sites and the remaining nuclei are located at sites whose oxygen environment is similar to that in stabilized hafnium oxide experiencing an interaction frequency very close to that in monoclinic  $\text{HfO}_2$ . Even in the tetragonal phase of the sample a definite value of asymmetry parameter  $\eta_1 = 0.32$  shows that the local structure is orthorhombic.

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