Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Physica B 389 (2007) 185–188
PHYSICA B
www.elsevier.com/locate/physb

Electric field gradients at ^{181}Ta sites in HfO$_x$

G.N. Darriba[a,b,*], A.M. Rodríguez[a,b], H. Saitovitch[c], P.R.J. Silva[c], A.F. Pasquevich[a,d]

[a]*Departamento de Física, Facultad de Ciencias Exactas, UNLP, Argentina*
[b]*Consejo Nacinal de Investigaciones Científicas y Técnicas, Argentina*
[c]*Centro Brasileiro de Pesquisas Físicas, Rio de Janeiro, Brasil*
[d]*Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, Argentina*

Abstract

In the present work we report preliminary results about the possibility to study properties of the order–disorder transition in HfO$_x$ solid solutions via the determination of the electric field gradient (EFG) at ^{181}Ta radioactive probes. Oxygen solution into the metal was achieved by arc melting stoichiometric amounts of metallic Hf and HfO$_2$ under argon atmosphere. Samples of HfO$_x$ with $x = 0.1$ and 0.2 were prepared. Two types of samples were used for the perturbed angular correlation (PAC) experiments by doping alternatively with ^{181}Ta, by neutron irradiation, the metallic Hf or the hafnium oxide. The PAC results on both samples were identical, with disappearing hyperfine signals of the metal and the oxide, showing a complete diffusion of the probes independent of the way of doping. The PAC signal of the HfO$_x$ solid solution consisted in a wide distribution of EFGs due to the oxygen disorder. This scheme held even after long thermal treatments at high temperature (several days at 1273 K). Annealing treatments at moderate temperature (600 K) were also made. In these cases the samples were cooling at a very low rate. These results, together with those obtained by measuring samples below and above the order temperature are reported.

PACS: 64.60.Cn; 82.80.Ej

Keywords: Electric field gradients; Phase transitions; Order—disorder

---

1. Introduction

It is known that the interstitial oxygen atoms dissolved in titanium [1] and zirconium [2] metals form ordered structures at low temperatures and cause order–disorder transitions between 600 and 800 K. Hafnium also belongs to the same IVA group as titanium and zirconium metals. Oxygen dissolves in hafnium metal up to 20 at% (O/Hf = 0.25) [3,4] and these dissolved interstitial oxygen atoms form ordered structures similar to those of titanium- and zirconium–oxygen solid solutions [5]. Hirabayashi et al. [6] determined the ordered structures of hafnium–oxygen solid solutions, HfO$_x$, by using electron and neutron diffraction methods. They reported that the basic ordered structures of HfO$_x$ was the ordered one for $x = \frac{1}{6}$ and oxygen vacancies for $x < \frac{1}{6}$ or interstitial oxygen atoms for $x > \frac{1}{6}$ existed in the basic ordered structure, as show in Fig. 1. Kato et al. measured heat capacities of hafnium oxygen solid solutions, HfO$_x$ ($x = 0.11$, 0.19 and 0.22) from 325 to 905 K and computed the entropy changes due to the order–disorder transition of oxygen sublattice from heat capacity data [7]. They discuss, in some detail, the order–disorder transition mechanism. We understood that perturbed angular correlation (PAC) experiments can give important new information about the distributions of the oxygen ions at both sides of the phase transition. This technique is appropriate for determining the interaction between the nuclear quadrupole moment of probe radioactive atoms located at lattice sites and the electric field gradients (EFG) produced by the ions in the neighborhood. Additionally, the isotope ^{181}Hf, quite adequate for PAC experiments, can be introduced in the compound as a

---

[*] Corresponding author. Departamento de Física, Facultad de Ciencias Exactas, UNLP, Argentina. Tel.: +54 221 4246062; fax: +54 221 4252006.
E-mail address: darriba@fisica.unlp.edu.ar (G.N. Darriba).

0921-4526/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2006.07.053

normal constituent. In the present paper, first results obtained under different conditions of concentration, annealing history and temperature are reported.

2. Experimental

Hafnium–oxygen alloys with O/Hf ratios of 0.1 and 0.2 were prepared as follows: hafnium metal ingot and hafnium oxide were mixed in appropriate ratios and melted a few times using an arc furnace under an argon atmosphere. ^{181}Hf activity was introduced in the samples during the preparation. Two different procedures were adopted. In samples hereafter labeled "a", the activity was introduced by doping with radioactive hafnium oxide, previously activated by thermal neutron irradiation. In samples labeled "b", the activity was introduced using metallic hafnium previously activated. The obtained samples were sealed in evacuated silica tubes, annealed for several days at 1273 K to homogenize the oxygen dissolved in the sample and cooled to room temperature (RT). Samples without radioactivity were prepared for X-ray diffraction characterization. PAC spectra were recorded at RT after several annealings at 1273 K and at different measuring temperatures. A standard PAC setup with four BaF_2 detectors arranged in a planar 90–180° geometry was used. Twelve coincidence spectra were simultaneously recorded. The system had a time resolution of 700 ps.

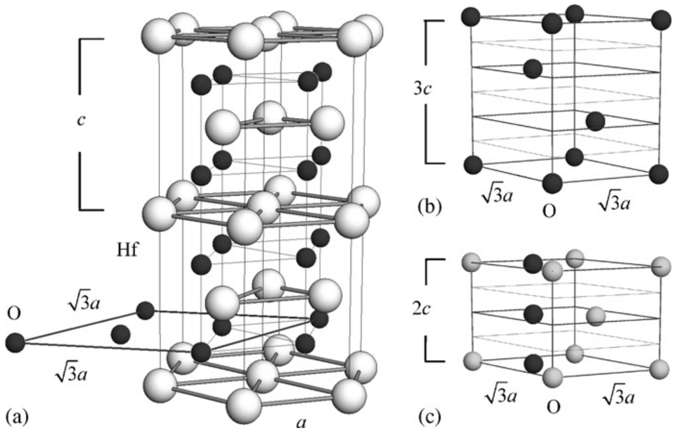

Fig. 1. (a) All possible positions of oxygen atoms (black atoms) in the HCP hafnium lattice (gray atoms). (b) Order structure of oxygen atoms (black atoms) for $x=\frac{1}{6}$, for $x<\frac{1}{6}$ these are the positions of oxygen vacancies and (c) interstitial oxygen atoms (black atoms) for $x>\frac{1}{6}$.

For a static quadrupole interaction the perturbation factor has the form

$$G_2(t)=\sum_{n=0}^{3} s_{2n}\, e^{-\delta\omega_n t}\, cos(\omega_n t).$$

The frequencies ω_n are related to the quadrupole frequency $\nu_Q = eQV_{zz}/h$ by $\omega_n = g_n(\eta)\nu_Q$. The coefficients s_{2n} and $g_n(\eta)$ are known functions of the asymmetry parameter $\eta=[V_{xx}-V_{yy}]/V_{zz}$, where V_{ii} denote the principal components of the EFG tensor. Theoretical perturbation factors of the form $A_2G_2(t)$ folded with the measured time resolution curve are fitted to the experimental functions. The exponential term accounts for a distribution of the EFG components of width δ. The

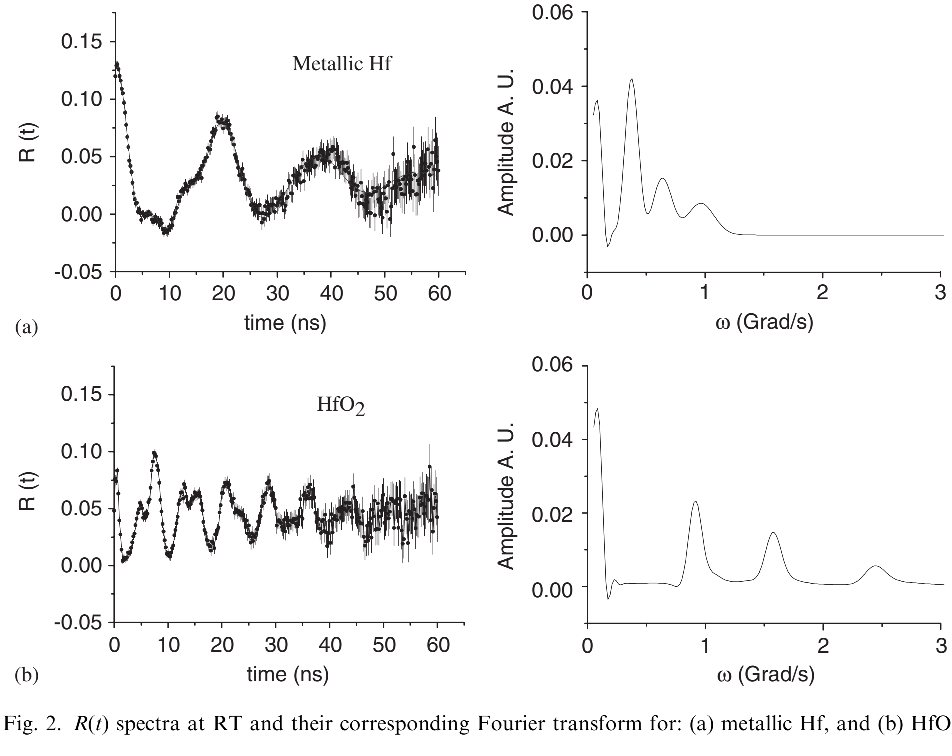

Fig. 2. $R(t)$ spectra at RT and their corresponding Fourier transform for: (a) metallic Hf, and (b) HfO_2

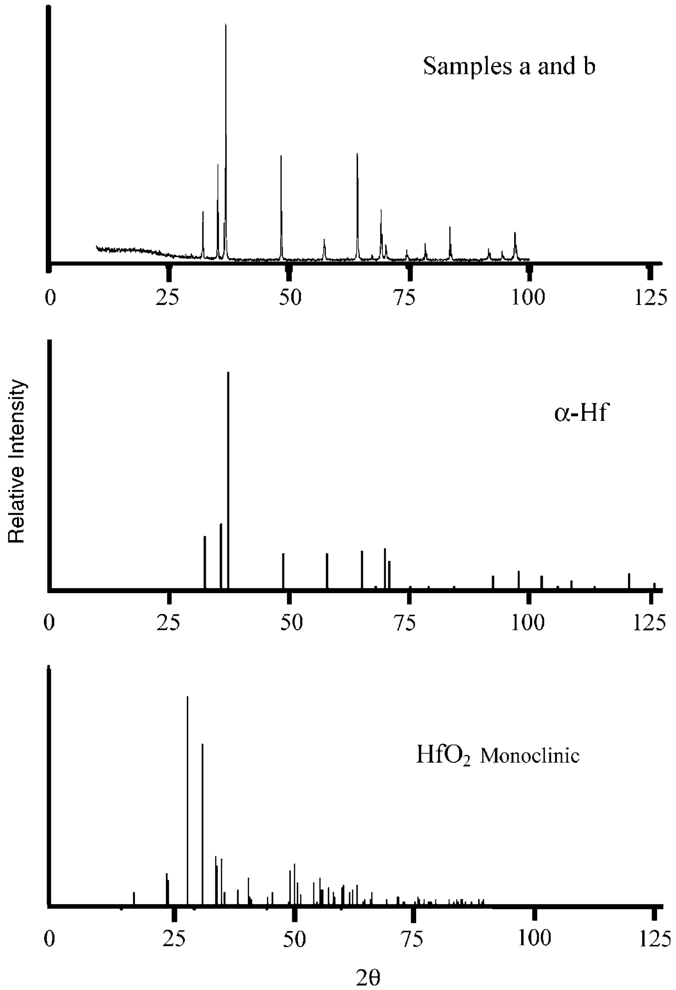

Fig. 3. Comparison between the X-ray diffraction patterns for samples a and b, α-Hf and monoclinic HfO_2 diffraction pattern, respectively, are given for comparison.

frequencies can also be obtained by Fourier analysis. The spectra are Fourier transformed as described elsewhere [8].

3. Results and discussion

In order to characterize the materials used in the preparation of the samples, PAC spectra of pure metallic hafnium (Fig. 2a) and hafnium oxide (Fig. 2b) were obtained. As was expected, the spectrum corresponding to ^{181}Ta in metallic hafnium, shows the characteristic frequency $\nu_Q \approx 320$ MHz and $\eta = 0.3$ [9], and the normal texture found in hafnium wires. The η value 0.3, obtained in spite of the HCP structure of metallic hafnium is a feature very well known [10], which will make difficult the comparison of the experimental results with simple point charge calculations. The RT spectrum of ^{181}Ta in hafnium oxide is characterized by the values $\nu_Q = 787$ MHz and $\eta = 0.38$, in good agreement with data in the literature [11].

X-ray diffraction pattern of a sample of HfO_x with $x = 0.2$ "as melted" is shown in Fig. 3. The expected diffraction lines for metallic hafnium and for hafnium oxide (monoclinic structure) are indicated in the same figure. As we see, the obtained pattern corresponds to metallic hafnium. It is an indication that either oxygen has disappeared or it is diluted interstitially in the metal. This ambiguity is removed with PAC experiments carried out with samples (type a and b), corresponding to the same concentration $x = 0.2$, and to the condition "as melted". The PAC spectra and its Fourier transforms are shown in Fig. 4. In fact, the PAC spectra do not correspond to pure metallic hafnium. This indicates that the oxygen ions are into the sample. Also it is worth to point out that both ways of preparation produced the same result: it does not matter

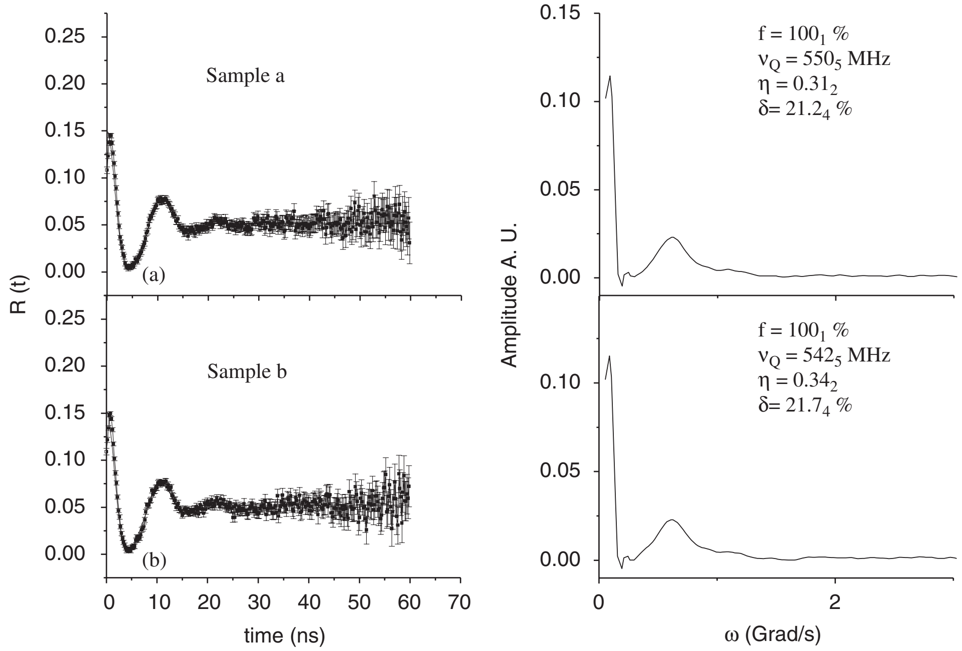

Fig. 4. $R(t)$ spectra at RT and their corresponding Fourier transform for $HfO_{0.2}$ (a) sample a and (b) sample b. The corresponding hyperfine parameters are displayed in the figure.

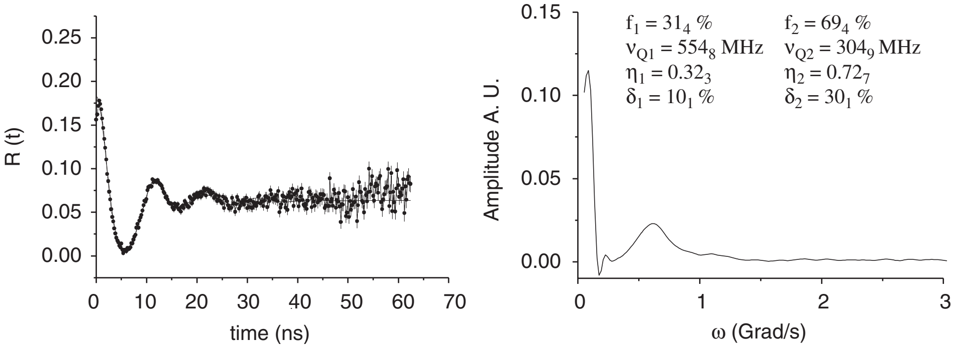

Fig. 5. $R(t)$ spectra at RT and their Fourier transform for $HfO_{0.1}$. The parameters of the hyperfine interactions are displayed in the figure.

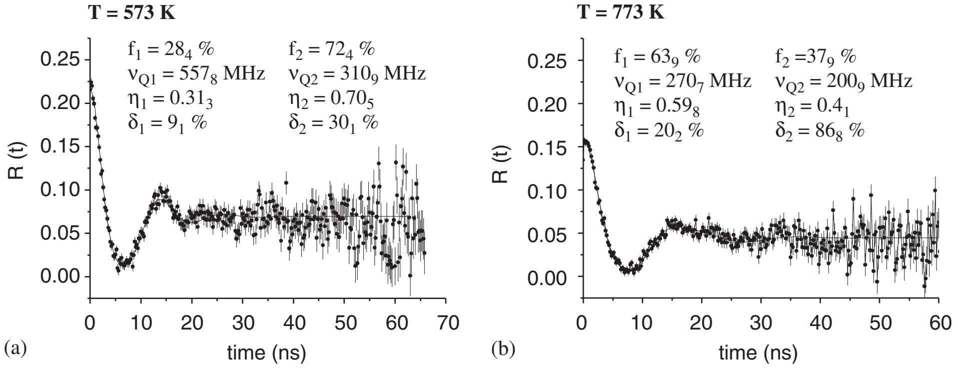

Fig. 6. $R(t)$ spectra for $HfO_{0.1}$ at (a) $T = 573$ K and (b) $T = 773$ K. The corresponding hyperfine parameters are displayed in the figure.

where the probes were localized at the beginning, they end at sites surrounded by a distribution of oxygen. In both cases the distribution has similar characteristics as can be inferred for the similitude of the hyperfine parameters (given for both samples in Fig. 4).

Samples with $x = 0.1$ were prepared by adding inactive hafnium to the samples with $x = 0.2$. The addition was accomplished by melting the materials again. A PAC spectrum is shown in Fig. 5. As we see, the dilution produces the decrease in the population and distribution of the already-existing interaction and the appearence of a new distributed interaction.

The samples were annealed several times in argon atmosphere at 1273 K, accumulating at the end 72 h of annealing. These treatments did not change the oxygen distributions. In the case of $x = 0.2$, annealing was made for two weeks at 600 K and very slow cooling (one week) until RT. This treatment decreased the distribution of EFGs.

Finally we have also carried out measurements at different temperatures (for $x = 0.1$), trying to see if the PAC method was sensible to the expected order–disorder transition. In Fig. 6 two spectra are shown, taken at both sides of the transition. For $T = 573$ K (under the transition temperature) the hyperfine parameters are basically the same as those measured at RT. For $T = 773$ K (over the transition temperature) the hyperfine parameters change, diminishing notably the quadrupole frequencies and increasing the distribution of both interactions.

4. Conclusion

It was shown that the PAC spectra are sensible to the oxygen distribution and to the measurement temperature. Computer simulations, in order to compare the experimental EFGs distributions with those arising from specific oxygen distributions, are underway. Also, experiments with concentrations near $x = 0.1666$ will be carried out. An ordered distribution of oxygens is expected at this concentration and consequently a well defined hyperfine interaction must be observed.

References

[1] T. Tsuji, M. Sato, K. Naito, Thermochim. Acta 163 (1990) 279.
[2] T. Tsuji, M. Amaya, K. Naito, J. Therm. Anal. 38 (1992) 1817.
[3] R.F. Domagala, R. Ruh, ASM Trans. Q. 58 (1965) 164.
[4] E. Rudy, P. Stecher, J. Less Common Met. 5 (1963) 78.
[5] G. Boureau, P. Gerdanian, J. Phys. Chem. Solids 45 (1984) 14l.
[6] M. Hirabayashi, S. Yamaguchi, T. Arai, J. Phys. Soc. Japan 35 (1973) 473.
[7] T. Kato, T. Tsuji, J. Nucl. Mater. 247 (1997) 98.
[8] A.N. Scian, E.F. Aglietti, M.C. Caracoche, P.C. Rivas, A.F. Pasquevich, A.R. López García, J. Am. Ceram. Soc. 77 (1994) 1525.
[9] R. Vianden, Hyperfine Interactions 15/16 (1983) 1081.
[10] J. Berthier, P. Boyer, J.I. Vargas, in: Hyperfine Interactions in Excited Nuclei, vol. 2, Gordon and Breach, New York, 1971.
[11] A. Ayala, R. Alonso, A. López García, Phys. Rev. B 50 (1994) 3547; J. Shitu, A.F. Pasquevich, J. Phys: Condens. Matter 9 (1997) 6313.