

TDPAC INVESTIGATION ON THERMALLY RELATED $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ and HfO_2

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The hyperfine quadrupole interaction of $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ at Hf sites is investigated from 14 to 820 K. No transitions have been found. After the complete dehydration of this compound at 393 K, chemical reactions take place which give rise to hafnium oxifluorides and metastable forms of hafnium oxide. Heating treatments at increasing temperatures make HfO_2 turn into its monoclinic phase.

1. Introduction

Following our hyperfine study of hafnium tetrafluorides, in this paper we present the thermal history of $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ between 14 and 820 K. In the first investigation [1] we reported the dehydration of this compound at 330 K and its further hydration at room temperature with a rate constant $k = (0.49 \pm 0.10)\text{d}^{-1}$. We also inferred that in these processes $\text{HfF}_4 \cdot \text{H}_2\text{O}$ played the role of an intermediate compound.

The present results have mainly been obtained by measuring the quadrupole hyperfine interaction as a function of temperature by means of the time differential perturbed angular correlations technique (TDPAC). Some X-ray powder diffraction diagrams at room temperature and thermogravimetric and differential thermal analysis (TGA and DTA) between 293 and 1273 K have also been performed in order to give better support to our conclusions.

Crystalline structures of $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ and HfF_4 have already been reported [2,3].

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2. Experimental

This work has been carried out using several samples of $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ prepared in our laboratory and one of HfF_4 commercially available. Once the former dehydrated to HfF_4 , we found no differences among the samples investigated, as they all suffered the same changes with temperature.

Powder samples of $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ were synthesized crystallizing HfO_2 in 40% HF and were then identified by X-ray diffraction analysis. The HfF_4 sample was supplied by Alfa Products [4]. All of them were encapsulated in 0.5 cm^3 sealed quartz tubes at atmospheric pressure and neutron irradiated at the Comisión Nacional de Energía Atómica (Argentina). The ^{181}Hf activity produced gave rise to the efficient 133–482 keV γ – γ cascade of ^{181}Ta used in this work as a TDPAC probe.

The high resolution TDPAC setup ($2\tau = 0.75 \text{ ns}$ at Hf energies), data handling and further procedure have been described elsewhere [5].

To take into account the possibility of several crystalline surroundings of the ^{181}Ta probes, a superposition of perturbation factors:

$$G_2(t) = \sum_i f_i G_2^i(t) \quad (1)$$

was assumed, where $G_2^i(t)$ are associated to the static quadrupole interactions in polycrystalline samples:

$$G_2^i(t) = \sigma_{20}(\eta_i) + \sum_{n=1}^3 \sigma_{2n}(\eta_i) \exp(-\delta_i \omega_{ni} t) \cos(\omega_{ni} t), \quad (2)$$

and the coefficients f_i were interpreted as the relative populations of each site.

A least squares fit of this theoretical function to the experimental data allowed us to determine the hyperfine quadrupole parameters already defined in ref. [1]: the quadrupole frequency ω_{Qi} , the asymmetry parameter η_i and the distribution width of frequencies δ_i which characterize the electric field gradient (EFG) acting at each site.

An appropriate heating system attached to the sample holder and a helium closed cycle cryogenic system were employed to achieve, in situ, the desired temperature within an uncertainty of $\pm 1 \text{ K}$.

3. Results

Figure 1 contains the most relevant hyperfine information which was drawn from our TDPAC measurements.

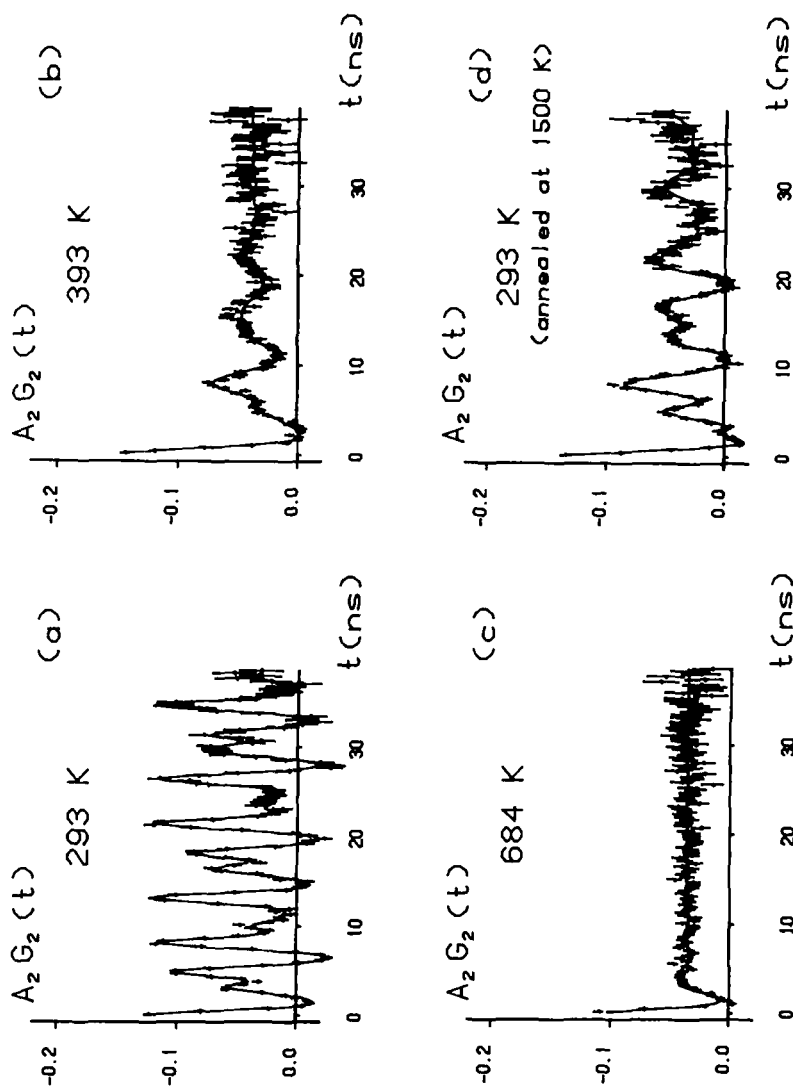


Fig. 1. Spin rotation curves related to the main changes observed during $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ thermolysis. Full lines are the fitted curves.

The spectrum plotted in fig. 1(a) showed the typical and well-defined hyperfine pattern of $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$, in agreement with that already published [1]. Between 14 and 293 K this compound exhibited a continuous evolution of the η parameter from 0.63 ± 0.01 at 14 K to 0.43 ± 0.01 at 293 K, accompanied by a slight decrease of the interaction frequency. The behaviour of the hyperfine interaction in the 293–360 K range agreed well with that reported in ref. [1].

At 393 K, when the TDPAC spectrum indicated that the unique interaction acting on the probes was that of HfF_4 [fig. 1(b)], the DTA presented the first endothermic peak. As the temperature increased, this interaction was gradually replaced by another one widely distributed. At 684, 730 K and at a subsequent room temperature measurement, the spin rotation curve was that shown in fig. 1(c). The fitted quadrupole parameters for the 684 K measurement were: $\omega_Q = (213 \pm 8) \text{ Mrad s}^{-1}$, $\eta = (0.44 \pm 0.04)$ and $\delta = (26 \pm 2)\%$. It is worth mentioning that the spectra so characterized exhibited both a slight loss of the anisotropy $A_2 G_2(0)$ and an apparent constant contribution to the perturbation factor. The first of these effects is generally associated with the inability of the equipment to efficiently resolve a rather high frequency, while the second one relates to some fraction of ^{181}Ta surroundings of cubic symmetry. Regarding complementary information, we can report that at a somewhat lower temperature, approximately centered at 623 K, a second endothermic peak was observed in the DTA, while the TGA showed an apparent loss of weight. In addition, a room temperature X-ray diagram on a portion of the active sample revealed the presence of a non-crystalline substance, but also exhibited the characteristic lines reported in ref. [6] for the HfO_2 cubic phase and those for Hf_2OF_6 in ref. [7].

Least squares fits of measurements at 798 and 820 K indicated that the relative fraction of the frequency distribution gradually diminished, giving rise to increasing fractions of the already known hyperfine interaction corresponding to monoclinic HfO_2 [8], and also to another one (relative fraction of 5%) characterized by $\omega_Q = (120 \pm 3) \text{ Mrad s}^{-1}$, $\eta = (0.78 \pm 0.04)$ and $\delta = (3 \pm 7)\%$.

Our heating system was not suitable for measuring at higher temperatures. Then, measurements at room temperature after off-line annealing for four hours at 960, 1000, 1200 and 1500 K were performed. All of them revealed the presence of three interactions whose fitted quadrupole parameters after heating at 1500 K [fig. 1(d)] were: $f_1 = (67 \pm 3)\%$, $\omega_{Q1} = (123 \pm 1) \text{ Mrad s}^{-1}$, $\eta_1 = (0.32 \pm 0.01)$, $\delta_1 = (4 \pm 1)\%$ (the monoclinic HfO_2 interaction); $f_2 = (18 \pm 2)\%$, $\omega_{Q2} = (127 \pm 1) \text{ Mrad s}^{-1}$, $\eta_2 = (0.72 \pm 0.02)$, $\delta_2 = (3 \pm 1)\%$ (assumed to be the same interaction which appeared at 798 K), and $f_3 = (15 \pm 3)\%$, $\omega_{Q3} = (219 \pm 2) \text{ Mrad s}^{-1}$, $\eta_3 = (0.86 \pm 0.02)$ and $\delta_3 = (3 \pm 1)\%$.

A subsequent X-ray powder diagram of the active sample revealed undoubtedly the presence of monoclinic HfO_2 , but also the principal lines of those reported by Rickard and Waters for the compound $\text{Hf}_3\text{O}_2\text{F}_8$ [7].

Finally, we can state that the total loss of weight determined from the TGA, between 293 and 1273 K, showed an excellent agreement with the calculated loss involved in the $\text{HfF}_4 \cdot 3\text{H}_2\text{O} \rightarrow \text{HfO}_2$ transformation.

4. Discussion and conclusions

The thermal evolution of the hyperfine interaction determined in $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ allows us to state that this compound presents no phase transitions above 14 K. The continuous change of ω_Q and η can not be explained until the behaviour of the crystalline structure of this compound as a function of temperature is known.

As reported in ref. [1], the $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ begins its dehydration above 330 K. In this work we achieved anhydrous hafnium tetrafluoride at 393 K. This confirms the conclusion of our previous work that $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ loses all its water molecules before any other reaction can take place, in disagreement with Rickard and Waters' observations [7].

Since the hydrogen positions in the $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ crystalline unit cell are not known, theoretical estimates of the EFG for this compound were not possible. However, point-charge model calculations could be performed for the HfF_4 crystalline lattice, for which all atomic positions in the unit cell at room temperature are known [3]. Experimental and calculated values for the major component of the EFG, V_{zz} , and the asymmetry parameter η show an excellent agreement if only the nearest neighbours to the Hf ion, i.e. the eight coordinated oxygen ions, are taken into account in the calculation. The comparison between the determined values at room temperature

$$V_{zz}^{\text{exp}} = (12.1 \pm 0.1) \times 10^{17} \text{ V cm}^{-2}, \quad \eta^{\text{exp}} = (0.37 \pm 0.02)$$

$$V_{zz}^{\text{calc}} = 13 \times 10^{17} \text{ V cm}^{-2}, \quad \eta^{\text{calc}} = 0.36$$

supports the idea of a highly ionic character for the lattice bonds of anhydrous hafnium tetrafluoride.

The loss of weight observed in the TGA when the DTA shows an endothermic peak at 623 K, along with the complete and irreversible change of the hyperfine pattern at 684 K, suggested that a chemical reaction had taken place, a result of which, as revealed by the X-ray diagram, cubic HfO_2 , Hf_2OF_6 and an amorphous substance were produced. Besides, the large interaction frequency distribution ($\delta = 26\%$) fitted for the spin rotation curve obtained at 684 K can be associated to the presence of the amorphous compound (see ref. [9]).

It has been reported that HfO_2 , of monoclinic structure at room temperature, turns reversibly into a tetragonal phase at 2173 K and finally undergoes a tetragonal to cubic change, also reversible, at approximately 2973 K [10]. Under certain circum-

stances, these high temperature phases have been found to exist as metastable ones at room and moderate temperatures. In fact, El-Shanshoury et al. [6], studying films of hafnium oxide at room temperature, identified a mixture of amorphous and cubic HfO_2 when annealing below 773 K, a mixture of the cubic and monoclinic phases when annealing between 800 and 1073 K and, annealing above the latter temperature, the monoclinic form of HfO_2 . This information led us to infer that the amorphous substance was HfO_2 . On the other hand, the sample thermal behaviour evidenced by the DTA from 623 to 723 K appeared quite analogous to the one reported during the heating of $\text{Zr}(\text{OH})_4$ [11] which, in a temperature range very similar to ours, presented the couple of endo—exothermic peaks corresponding to the occurrence of amorphous ZrO_2 and to its subsequent crystallization into the metastable tetragonal phase, respectively.

Based on the arguments just exposed, we identified the spectrum obtained at 684 K with the hyperfine interactions corresponding to amorphous HfO_2 , cubic HfO_2 and Hf_2OF_6 . The observed constant contribution to the spin rotation curve may be explained under the hypothesis that hafnium surroundings in cubic HfO_2 had the lattice cubic symmetry. If this were so, the highly distributed frequency fitted should be associated to the existence of the two remaining compounds. Concerning the observed reduction of anisotropy, probably the lack of crystallinity of part of the system could account for it, since strong interactions may then be expected.

The further occurrence of monoclinic HfO_2 at 798 K supports our above speculations about the identification of the amorphous substance as HfO_2 . Indeed, other authors [11] have reported, after heating $\text{Zr}(\text{OH})_4$ at increasing temperatures, and previous to the appearance of the monoclinic phase, the existence of the amorphous state and the metastable tetragonal phase of ZrO_2 , isomorphous of HfO_2 .

Hence, we conclude that the last hyperfine change observed [fig. 1(d)] represents the final step in the crystallization of amorphous HfO_2 into the monoclinic phase, known as the stable form of HfO_2 between 293 and 2173 K.

We have not achieved, with the off-line thermal treatments at temperatures higher than 820 K and subsequent measurements at 293 K, the 100% population of monoclinic HfO_2 . After the last annealing at 1500 K, we determined a relative fraction of 67%, the remaining 33% being nearly equally distributed in two additional interactions. As the X-ray powder diagram evidenced the presence of only two compounds, monoclinic HfO_2 and $\text{Hf}_3\text{O}_2\text{F}_8$, the idea of assigning the extra interactions to non-equivalent sites for hafnium atoms in the hafnium oxifluoride molecule was tempting. Nevertheless, these two interactions were observed to appear not simultaneously and with a different population evolution as measurement or annealing temperature increased. This fact led us to infer that only one of them had to be assigned to the $\text{Hf}_3\text{O}_2\text{F}_8$ lattice, the other one remaining unidentified. It is worth noting at this point that, when observing by electron diffraction ultra-high purity submicron ZrO_2 powder prepared by thermal decomposition of Zr salts [12], the tetragonal meta-

stable phase is found at room temperature. We wonder whether the third TDPAC component might be associated to the metastable tetragonal phase of HfO_2 , the structure of which, as well as the X-ray powder diagram, are not yet known.

With the aim of elucidating this situation, we performed a TDPAC measurement at room temperature on a puriss HfO_2 sample acquired from Fluka [13] and obtained the spin rotation curve shown in fig. 2. To our surprise, in addition to the

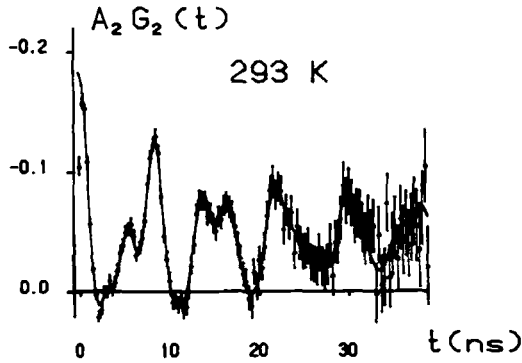


Fig. 2. TDPAC spectrum of puriss HfO_2 . The full line corresponds to the fitted curve.

well-known unique interaction frequency corresponding to HfO_2 , the high resolution coincidence setup employed was able to detect the same two interactions which accompanied the HfO_2 produced by thermolysis, though in very low proportions. The fitted quadrupole parameters in this case were:

$$f_1 = (87 \pm 3)\% \quad \omega_{Q1} = (124 \pm 1) \text{ Mrad s}^{-1} \quad \eta_1 = (0.35 \pm 0.01) \quad \delta_1 = (3 \pm 1)\%$$

$$f_2 = (7 \pm 2)\% \quad \omega_{Q2} = (143 \pm 4) \text{ Mrad s}^{-1} \quad \eta_2 = (0.75 \pm 0.05) \quad \delta_2 = (3 \pm 3)\%$$

$$f_3 = (6 \pm 2)\% \quad \omega_{Q3} = (218 \pm 2) \text{ Mrad s}^{-1} \quad \eta_3 = (0.89 \pm 0.02) \quad \delta_3 = (1 \pm 1)\%.$$

The similarity between figs. 1(d) and 2 is remarkable, though when observing the relative peak intensities, the latter shows a hyperfine pattern closer to the one typical for HfO_2 . It is interesting to notice that Koićki and co-workers [8] have found that post irradiation annealings at increasing temperatures improved the detailed structure of the TDPAC pattern of HfO_2 , although they declared they did not investigate whether the annealing healed the possible effect of neutron irradiation or defined the

structure of HfO_2 better. With the idea that no relevant radiation damage is present in our sample, further measurements on HfO_2 are in progress in order to obtain more information about the spurious interactions observed and to analyze the conditions under which the 100% monoclinic HfO_2 can be reached.

In analogy with some reports in the literature [14], no annealing treatment was necessary to obtain the TDPAC spectrum shown in fig. 2. We do not understand either the situation described by other authors [15] which needs thermal treatments at high temperatures (greater than 1000 K), or the complete loss of anisotropy seen by Salomon et al. [16]. Although Gerdaus's group assumes the existence of radiation damage previous to the annealing treatment and Salomon et al., on the other hand, explain their results as being due to after-effects, both investigations report qualitatively the same physical situation: without any annealing, the anisotropy drops abruptly within approximately five nanoseconds. We observed the same experimental fact at 684 K [see fig. 1(c)], where a subsequent room temperature X-ray analysis indicated the presence of an amorphous compound which was identified as HfO_2 . We think this is not a mere coincidence, but rather that the results obtained by those authors may perhaps be better understood by assuming that the as-prepared samples were not crystallized HfO_2 .

Finally, we want to point out that the identification of the hafnium oxides was done using the diffraction data reported by Rickard and Waters [7], and is subject to the fact that the empirical formulae they give have no structural significance.

On the basis of the preceding discussion we are able to sum up some conclusions:

- (i) The compound $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ presents no phase transitions.
- (ii) The dehydration of $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ leads to $\text{HfF}_4 \cdot \text{H}_2\text{O}$ and HfF_4 . The spin rotation curves of both dehydration products appear as rather distributed interaction frequencies ($\delta \sim 10\%$). At 393 K, the dehydration is completed. The excellent agreement between the experimental and calculated EFG values for HfF_4 clearly evidences the ionic nature of the chemical bonds between the central Hf^{+4} ion and its coordinated F^- ions.
- (iii) HfF_4 gives rise to, with increasing temperature, the irreversible production of hafnium oxide and Hf_2OF_6 , the corresponding TDPAC spectrum showing the typical pattern of a very wide frequency distribution.
- (iv) When produced via HfF_4 thermolysis, HfO_2 rises in the metastable amorphous and cubic forms.
- (v) When finally the monoclinic phase of HfO_2 crystallizes, its typical interaction is accompanied by two others. We could not decide which one corresponds to the compound $\text{Hf}_3\text{O}_2\text{F}_8$ revealed by the X-ray diffraction pattern. The same two additional interactions could be detected in very low proportions by our high resolution TDPAC setup in a puriss HfO_2 sample.

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