TDPAC CHARACTERIZATION OF $Ni_2HfF_8 \cdot 12H_2O$ AND ITS DECOMPOSITION PRODUCTS

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The hyperfine interaction in $Ni_2HfF_8 \cdot 12H_2O$ has been determined between 77 K and 1100 K by means of the time-differential perturbed angular correlation technique. From 200 K on, the one-site phase existing at lower temperatures undergoes a gradual phase transition until, at room temperature, the populations of both phases attain a 2:1 ratio. While the quadrupole frequencies characterizing them exhibit a $T^{3/2}$ thermal dependence, their population ratio seems to obey a Boltzmann distribution. At 350 K, when the η-value of the high temperature phase electric field gradient approaches its maximum value, the starting compound decomposes to $NiHfF_6 \cdot 6H_2O$. A kinetics study of the $Ni_2HfF_8 \cdot 12H_2O$ recovery at room temperature seems to indicate that a tri-dimensional diffusion mechanism is responsible for the corresponding reaction process. The first decomposition product of $NiHfF_6 \cdot 6H_2O$ left to atmospheric pressure is found to be $NiHfF_6 \cdot 4H_2O$ at 368 K and, between 414 K and 590 K, the high temperature cubic phase of $NiHfF_6$ and Hf_2OF_6 can be simultaneously observed. Finally, monoclinic HfO_2 appears from 1020 K on, having been preceded by an interaction which can be though of as depicting a preliminary stage in hafnia formation.

1. Introduction

In the last years, an important effort has been made in the field of solid state reactions through the investigation of oxidation and thermal decomposition processes, using conventional techniques. Recently, results obtained via the time-differential perturbed angular correlation (TDPAC) technique have been published with the double purpose of giving more light on the subject and of introducing a non-conventional technique in chemical reactions [1].

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This work was undertaken in order to obtain microscopic information about the thermal changes occurring in $Ni_2HfF_8 \cdot 12H_2O$ within the range 77 K and 1100 K. The available literature about this compound is poor. Davidovich et al. [2] reported the synthesis and X-ray diffraction lines of nickeloctofluorohafnate hydrate. They also observed that this compound was isomorphous with those of Co and Zn.

2. Experimental

$Ni_2HfF_8 \cdot 12H_2O$ was prepared following Davidovich et al. [2]. Once the compound was identified by X-ray analysis, the samples to be investigated were sealed in quartz tubes of 5 mm diameter and 50 mm long at atmospheric pressure.

Two different samples were irradiated to carry out this investigation, and each of them was analyzed at different temperatures covering the thermal ranges 77–300 K and 300–1100 K, respectively. Measurements below room temperature were performed in Rio de Janeiro.

^{181}Hf activity produced by thermal neutron irradiation of the compound populates the efficient 133–482 keV γ–γ cascade of ^{181}Ta used in this investigation as a TDPAC probe. A standard fast–slow two-detector set-up ($2\tau = 0.75$ ns at Ta energies) with CsF detectors and an electric furnace were used to obtain the experimental spin rotation curves between 300 K and 1100 K. Measurements for the range 77–300 K were made with a conventional fast–slow four-detector set-up with NaI(Tl) detectors, and the sample was mounted in a liquid-nitrogen cryostat with He gas flux.

The hyperfine quadrupole parameters corresponding to each interaction, i.e. the quadrupole frequency $\omega_Q = eQV_{zz}/4I\,(2I + 1)\hbar$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, the frequency distribution parameter δ and also the relative fractions f_i of probe nuclei subject to different quadrupole interactions, were obtained from the $A_2G_2(t)$ experimental curves using a nonlinear least-squares fitting program that took into account the finite time resolution of the equipment. For the time-dependent interactions found during this investigation, the Abragam and Pound model [3] of fast relaxation was satisfactorily used.

Although TDPAC has been the technique mainly used in this work, the results have been complemented with those from differential thermal and thermogravimetric analysis (DTA and TGA) performed in air at a heating rate of 6 K/min and 10 K/min, respectively, and with X-ray diffraction patterns. The latter were obtained at room temperature after heating inactive samples of $Ni_2HfF_8 \cdot 12H_2O$ to different temperatures.

3. Results and discussion

Figure 1(a) shows the TDPAC spectrum of $Ni_2HfF_8 \cdot 12H_2O$ taken at room temperature, which was fitted with the two interactions whose quadrupole parameters are listed in table 1, in a 2:1 ratio. When the sample was cooled to 77 K, only one interaction was needed to fit the experimental data (see fig. 1(b) and table 1). Upon
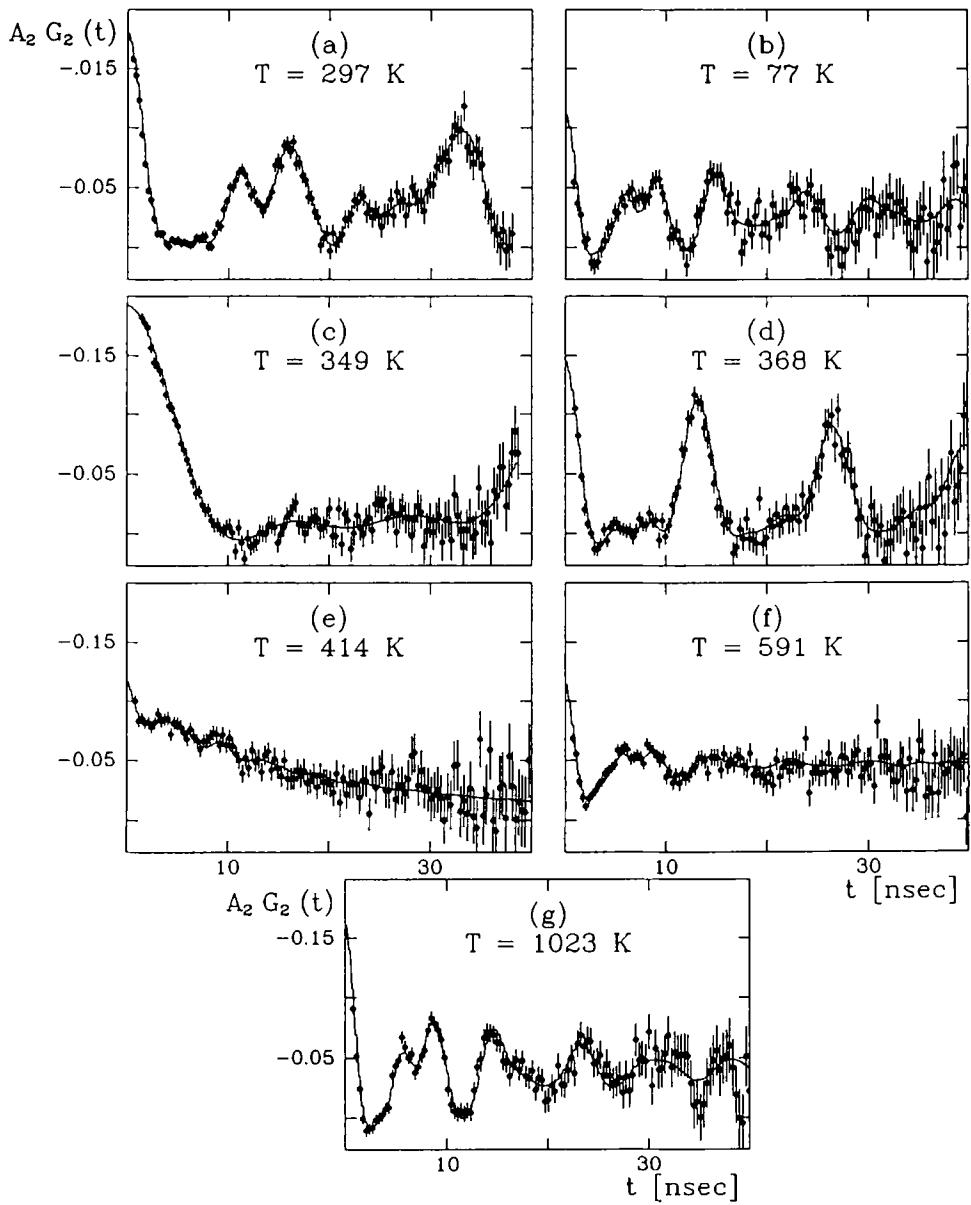
Fig. 1. Spin rotation curves obtained for $Ni_2 HfF_8 \cdot 12H_2O$ at different temperatures. Full lines are the fitted curves to the data. Differences in the initial anisotropies are due to different geometrical experimental conditions.

Table 1

Typical values of the quadrupole hyperfine parameters corresponding to the different compounds found during the thermal evolution of the $Ni_2HfF_8 \cdot 12H_2O$. The listed data correspond to temperatures where the relative fraction of each interaction was maximum

Compound	Tem. (K)	f (%)	ω_Q (Mrad/s)	V_{zz} (10^{17} V/cm^2)	η	δ
β-$Ni_2HfF_8 \cdot 12H_2O$	296	71_3	60.0_3	6.25_3	0.28_1	0.05_1
α-$Ni_2HfF_8 \cdot 12H_2O$		$29_\star$	85.0_4	8.85_4	0.13_3	0.01_1
α-$Ni_2HfF_8 \cdot 12H_2O$	77	$100_\star$	113.0_1	11.77_1	0.47_1	0.05_1
$NiHfF_6 \cdot 6H_2O$	350	$100_\star$	23.0_3	2.39_3	0.10_3	0.05_1
$NiHfF_6 \cdot 4H_2O$	368	$100_\star$	79.0_3	8.23_3	0.14_2	0.04_1
$NiHfF_6$	414	$74_\star$	$\lambda = (0.040 \pm 0.006)$ ns^{-1}			
Hf_2OF_6		26_4	171_8	17.8_8	$0.55_\star$	$0.17_\star$
HfO_2[a]	590	83_1	112_2	11.6_2	0.51_2	0.13_2
Hf_2OF_6		17_5	170_7	17.7_7	$0.68_\star$	$0.11_\star$
HfO_2[b]	1020	$100_\star$	114_6	11.8_6	0.44_1	0.07_1

[a]Preliminary stage of the monoclinic HfO_2 formation.
[b]Monoclinic phase.
★Fixed parameter.

gradual heating, this situation remained unchanged up to 200 K, the temperature at which the two interaction-picture reappeared. The additional interaction grew at the expense of the fraction observed at low temperatures, until at room temperature the interactions and relative fractions of the initial spectrum were recovered. This situation did not change up to 350 K. The replacement process between both interactions can be clearly seen in fig. 2, which also shows the thermal evolution of the quadrupole parameters involved in the range 77–350 K.

In the light of the present results and bearing in mind that there is no information about the crystalline structure of $Ni_2HfF_8 \cdot 12H_2O$, we have assumed that this compound crystallized at room temperature in a mixture of two phases in a 2:1 ratio. It then has to be assumed that the diffraction pattern presented by Davidovich [2] was a mixture of these two phases. Therefore, the change observed above 200 K was assigned to a reversible $\alpha \rightarrow \beta$ phase transition. It is interesting to notice at this point that, as it has already been observed for other phase transitions [4], the ratio of the relative fractions of both interactions obeys an Arrhenius behaviour (see fig. 3) from which an activation energy $E_a = (10.8 \pm 0.8)$ kJ/mol can be estimated.

The monotonous decrease of the two quadrupole frequencies of $Ni_2HfF_8 \cdot 12H_2O$ observed with increasing temperature was satisfactorily described by the function [5]

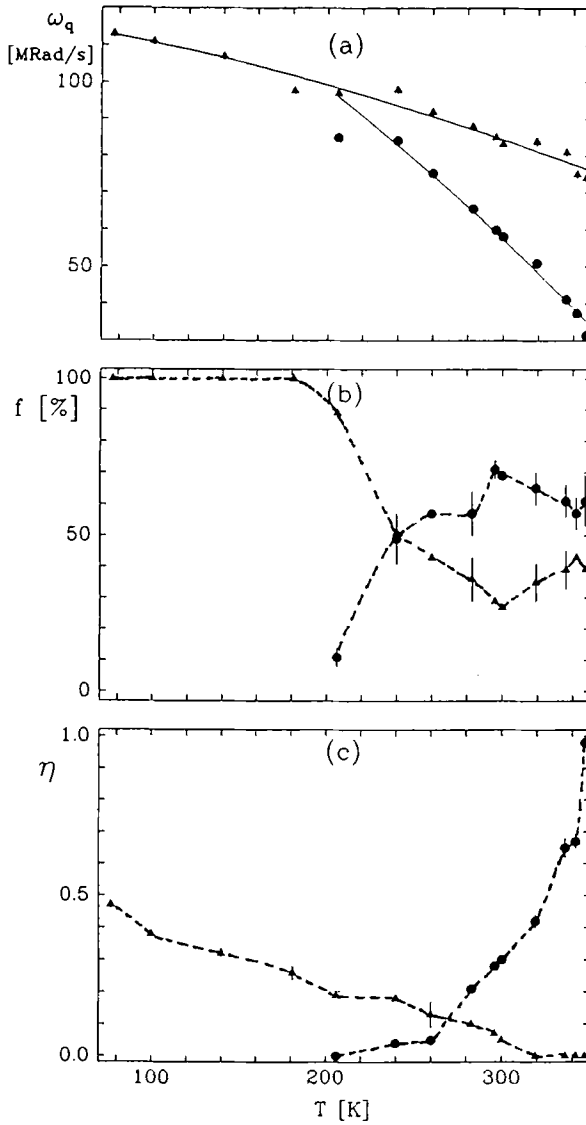$$\omega_Q(T) = \omega_Q(0) (1 - BT^{3/2}), \tag{1}$$

Fig. 2. Thermal evolution of the relative fractions and hyperfine parameters deduced from the fits between 77 K and 350 K. Two different symbols are used in order to show the evolution of each interaction. Full lines in (a) are the fitted curves. In (b) and (c), the dashed lines are a guide for the eye only.

which has been plotted as full lines in fig. 2(a). This dependence is known to work for metals, and it has also been observed in some dielectric lattices [6].

When the symmetry parameter of the high temperature phase approached its maximum value ($\eta \to 1$) at 350 K, the hyperfine pattern of $Ni_2HfF_8 \cdot 12H_2O$ suddenly

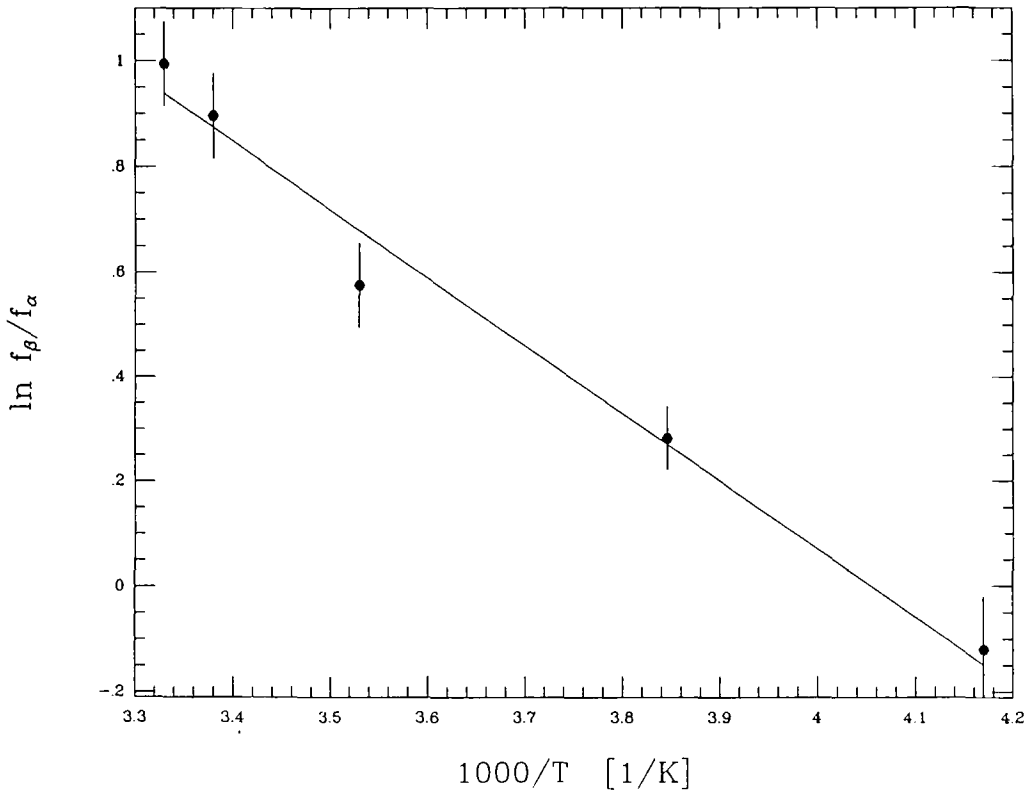Fig. 3. Logarithmic plot of the relative fraction ratio f_β/f_α in Ni$_2$HfF$_8$·12H$_2$O as a function of reciprocal temperature. f_α and f_β denote the low temperature phase and the high temperature phase relative fraction, respectively.

changed (fig. 1(c)) into the one corresponding to NiHfF$_6$·6H$_2$O, previously reported in a recent work [7], giving clear evidence of a decomposition process, and it can be supposed that this reflects the reaction

$$\text{Ni}_2\text{HfF}_8 \cdot 12\text{H}_2\text{O} \Leftrightarrow \text{NiHfF}_6 \cdot 6\text{H}_2\text{O} + \text{NiF}_2 + 6\text{H}_2\text{O}.$$
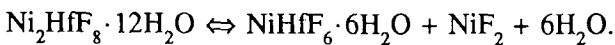
In order to investigate the reversibility of this reaction, the sample was then cooled to room temperature. The subsequent hyperfine pattern showed the presence of $(58 \pm 4)\%$ NiHfF$_6$·6H$_2$O and $(42 \pm 3)\%$ of the two phases of Ni$_2$HfF$_8$·12H$_2$O.

Suspecting that the kinetics of this process could be observed by the TDPAC technique, successive and independent room temperature measurements were performed. The time evolution of the relative abundance of the two phases of Ni$_2$HfF$_8$·12H$_2$O is shown in fig. 4. Several kinetic laws were attempted, but the best fit (full line in fig. 4) was achieved with an equation of the form:
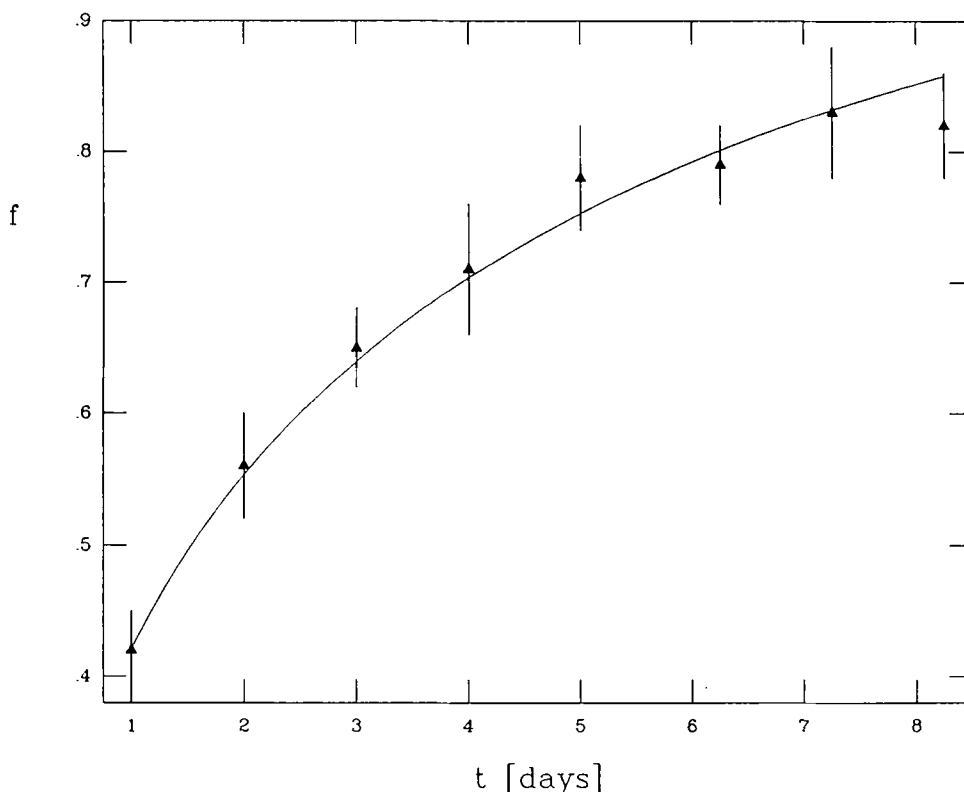
$$Kt = [1 - (1 - \alpha)^{1/3}]^2, \tag{2}$$

Fig. 4. Time evolution of the total relative fraction of $Ni_2HfF_8 \cdot 12H_2O$ at room temperature. The full line is the fitted curve.

which corresponds to a three-dimensional diffusion model [8], where K is the rate constant and α is the fraction of the product $Ni_2HfF_8 \cdot 12H_2O$ formed at time t. The value obtained for the rate constant was $K = (0.028 \pm 0.001) \, d^{-1}$.

Then, upon heating the samples to 350 K, $NiHfF_6 \cdot 6H_2O$, the starting compound of the kinetics study, reappeared. In order to obtain information about its thermal behaviour and to investigate its oxidation, the quartz tube was opened and measurements at room temperature and increasing temperature were performed.

At 368 K, the TDPAC pattern of $NiHfF_6 \cdot 6H_2O$ changed into the typical and well-defined hyperfine spectrum of $NiHfF_6 \cdot 4H_2O$ (fig. 1(d) and table 1), already determined (7). In the subsequent measurement, at 414 K, the spin rotation curve was fitted with two interactions (fig. 1(e) and table 1). One of them exhibits the dynamical characteristics previously associated with the cubic phase of $NiHfF_6$ [7] and the other one, with a relative intensity of $(26 \pm 4)\%$, corresponded to an EFG depicted by $\omega_Q = (171 \pm 8)$ Mrad/s, $\eta = 0.55$ (fixed), and $\delta = 17\%$ (fixed). This situation prevailed up to 580 K. An X-ray powder diagram taken at room temperature after heating an inactive sample at 511 K revealed the presence of $NiHfF_6$, Hf_2OF_6, and a small amount

of $NiHfF_6 \cdot 6H_2O$, the presence of which can be explained in terms of the high hydroscopicity of $NiHfF_6$. This information led us to infer that the interaction accompanying the cubic phase corresponds to the oxifluorohafnate.

A comparison with the thermal evolution of $NiHfF_6 \cdot 6H_2O$ [7] indicates that the low temperature phase of $NiHfF_6$, formed previously above 412 K, has not been observed in this work. Instead, at 414 K the high temperature phase has already appeared. This temperature, which is in better agreement with that of 458 K reported for the hexagonal-to-cubic phase transition in the anhydrous compound [9] using X-ray techniques, shows a thermal shift which may be attributed to the different experimental conditions attained in both experiments. Furthermore, also the $NiHfF_6 \cdot 4H_2O$ compound appeared here at a much lower temperature.

The $NiHfF_6$ was stable up to 580 K. From 590 K on, TDPAC spectra had to be fitted with two contributions, about 25% corresponding to Hf_2OF_6 and the rest showing a 15% distributed EFG of quadrupole frequency very similar to that of monoclinic HfO_2 but with an η-value somewhat higher (see fig. 1(f) and table 1). This situation remained unchanged until, at 1020 K, both interactions resolved into the typical spectrum of monoclinic HfO_2. Regarding the unidentified hyperfine interaction accompanying that of Hf_2OF_6, it had already been found during the oxidation process of another hafnium salt [10]. Furthermore, in a recent investigation on the thermal decomposition of $ZrO_2 \cdot 2H_2O$ [11], a very similar EFG has been determined to exist in a thermal range intermediate between the occurrence of amorphous zirconia and baddeleyite. The corresponding hyperfine interaction, observed only thanks to the microscopic nature and high resolution capacity of the TDPAC technique, was interpreted as being due to a preliminar stage in the formation of the stable monoclinic phase.

The losses of weight observed in the TGA, simultaneously with DTA endothermic peaks, were in good agreement with changes found during the TDPAC investigation. Nevertheless, the one interpreted as being due to the dehydration reaction $Ni_2HfF_8 \cdot 12H_2O \Rightarrow Ni_2HfF_8 \cdot 8H_2O + 4H_2O$ was not observed by the hyperfine method of the angular correlations. Since this change occurred only 10 K below the temperature of the subsequent decomposition to $NiHfF_6 \cdot 6H_2O$, it can be supposed that it had been by-passed during the sequence of experimental TDPAC measurements.

4.   Conclusions

On the basis of the preceding results, we can sum up the following conclusions:

(1) $Ni_2HfF_8 \cdot 12H_2O$ presents a thermal reversible and gradual phase transition beginning at 200 K, for which an activation energy of (10.8 ± 0.8) kJ/mol has been estimated.

(2)   The quadrupole frequencies associated to the two phases exhibit a $T^{3/2}$ temperature dependence.

(3)   The decomposition of $Ni_2HfF_8 \cdot 12H_2O$ leads to $NiHfF_6 \cdot 6H_2O$. A kinetics law considering a three-dimensional diffusion process is proposed for the reverse reaction and a rate constant $K = (0.028 \pm 0.001)$ d^{-1} has been derived.

(4)   The thermal behaviour of $NiHfF_6 \cdot 6H_2O$ in air has been investigated up to 1100 K. It has been decomposed to $NiHfF_6 \cdot 4H_2O$ at 368 K and to the high temperature phase of $NiHfF_6$ and Hf_2OF_6 at 414 K. The latter compounds oxidate at 1020 K into monoclinic hafnium oxide. Within the range 590–1000 K, the oxifluorohafnate was accompanied by a hyperfine interaction which was associated with a preliminar stage of the monoclinic HfO_2 formation.

Acknowledgements

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