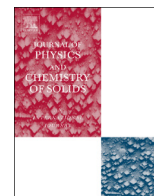




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Low temperature structural phase transition in hafnium and zirconium tetrafluoride trihydrates

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ABSTRACT

From time-differential perturbed angular correlation (TDPAC) measurements, the monoclinic and triclinic crystal structures in hafnium and zirconium tetrafluoride trihydrates are found to be present simultaneously in both the compounds. From previous TDPAC and XRD investigations, a monoclinic crystal structure for $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ but, for its analogues zirconium compound, a triclinic structure was reported. Contrary to earlier reports, the triclinic fraction in $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ is found to be maximum (80%) at room temperature. In fact, the triclinic crystal structure of $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ is reported here which was not known prior to this report. In $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$, a strong signal (80–90%) for the triclinic structure is found at room temperature while the monoclinic fraction appears as a weak signal (10–15%). Structural phase transitions in these trihydrate compounds have been observed in the temperature range 298–333 K.

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1. Introduction

The compounds of hafnium and zirconium with identical chemical compositions are expected to produce the same crystal structure due to very similar chemical properties of Hf and Zr and their identical crystal structures. It was found also that all compounds of hafnium and zirconium with same chemical compositions produce the same crystal structures. The only exception was in the case of hafnium tetrafluoride trihydrate and its analogue zirconium tetrafluoride trihydrate. In all other hafnium and zirconium compounds, similar values of quadrupole frequencies and asymmetry parameters were reported [1] from time-differential perturbed angular correlation (TDPAC) measurements which indicated their isostructural crystalline properties. Considering the compounds of hafnium and zirconium tetrafluoride trihydrates, a monoclinic polymeric structure was found for $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ [2]. On the other hand, the crystal structure of $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$ [3] was found to be triclinic and is formed from discrete dimeric $\text{Zr}_2\text{F}_8(\text{H}_2\text{O})_6$ groups in which the Zr atoms share the F...F common edge. In the polymeric structure of $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$, one of the H_2O molecules is not directly linked to the central Hf atom but is located between the chains [4]. The different crystal structure properties of these two trihydrate compounds of Hf and Zr are not understood and, therefore, it is of high interest to resolve the structure of these compounds. Considering this fact, further studies in the two

trihydrate compounds of hafnium and zirconium are worth spending. In this respect, TDPAC studies are useful where the electric field gradient (EFG) at the ^{181}Hf probe nuclear site can be determined with sufficient accuracies. The crystal structure environment surrounding the probe atom generates an EFG at the probe nuclear site if the crystal structure has a non-cubic symmetry. For a cubic symmetry, it produces zero EFG. Now, for the compounds of Hf and Zr, if nearly same values of EFG are produced at the probe site it indicates that these have same crystal structure environment. Thus, by comparing the TDPAC results, the isostructurality of the two compounds of Hf and Zr can be checked easily. Also, TDPAC is a sensitive technique to find any small EFG and very much helpful to determine the crystal structure with sufficient accuracy. Study of temperature dependence of EFG in a material is an excellent tool to determine the electron density that depends on chemical composition of materials.

The X-ray diffraction (XRD) method can also be employed for the crystal structure information quite accurately. XRD measurements in the hafnium tetrafluoride compounds were done earlier by Rickard and Waters [5]. From their measurements it was found that neither $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ nor $\text{HfF}_4 \cdot \text{H}_2\text{O}$ are isostructural with the analogous zirconium compounds. But, from recent XRD studies [4], a monoclinic modification of $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$ (β - $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$) is reported and it is shown that this monoclinic form of $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$ gives identical crystal structure parameters to that found in monoclinic $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$.

Previous TDPAC measurements [6–8] in these two Zr and Hf compounds reported widely different values of quadrupole frequency and asymmetry parameter. The compound $\text{HfF}_4 \cdot 3\text{H}_2\text{O}$ produced values of $\omega_Q = 203 \text{ Mrad/s}$, $\eta = 0.35$ [6] and these

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correspond to the monoclinic crystal structure (β -HfF₄·3H₂O). The compound ZrF₄·3H₂O, on the other hand, produced values of quadrupole frequency $\omega_Q \sim 183$ Mrad/s and asymmetry parameter $\eta \sim 0.83$ [7,8] and these were attributed to the triclinic crystal structure (α -ZrF₄·3H₂O). Therefore, previous results from TDPAC clearly indicate that ZrF₄·3H₂O and HfF₄·3H₂O have different crystal structures. In ZrF₄·3H₂O, no signal corresponding to its monoclinic structure was observed from earlier PAC measurements [7,8]. The XRD results by Davidovich et al. [4], however, indicate that both ZrF₄·3H₂O and HfF₄·3H₂O can have monoclinic structures and they really do not have different crystal structures as reported earlier. But, to the best of our knowledge, there is no report of triclinic structure in HfF₄·3H₂O (α -HfF₄·3H₂O). Since, finding the triclinic structure of HfF₄·3H₂O, if any, is of great importance to resolve the structures of HfF₄·3H₂O and ZrF₄·3H₂O, we have performed detailed TDPAC measurements in both these compounds. If the triclinic modification of HfF₄·3H₂O is also found, the iso-structurality of these two tetrafluoride trihydrates like other Hf and Zr compounds will be confirmed.

Apart from structural importance of HfF₄·3H₂O and ZrF₄·3H₂O, the anhydrous HfF₄ and ZrF₄ are shown to be optical coating materials [9] with excellent and stable transmission properties over the infrared region. It is, therefore, interesting to study the dehydration properties of these trihydrate materials with temperature and to check the stability of HfF₄ and ZrF₄ at room temperature. The temperature dependent PAC measurements are useful to find any structural phase transition or any chemical change in the sample with temperature.

2. Experimental details

The samples ZrF₄·3H₂O and HfF₄·3H₂O have been synthesized chemically. For the preparation of tetrafluoride zirconium compound, few milligrams of Zr (with $\sim 5\%$ Hf) procured from M/S Alfa Aesar is dissolved in concentrated HF (40%) to form a clear solution. A tiny drop of active Hf metal (¹⁸¹Hf) in concentrated HF is added to this solution and it is slowly dried at room temperature (~ 25 °C). Similarly, for the preparation of hafnium tetrafluoride trihydrate compound, a small piece of wire (~ 5 mg) of natural Hf metal (with 3–5% Zr) is dissolved in concentrated HF. A very small quantity of active solution of ¹⁸¹Hf in HF is added to it. This solution is dried slowly at room temperature till the solid crystal is formed. A natural Hf wire with $\sim 5\%$ Zr procured from M/S Alfa Aesar was activated by thermal neutron capture (flux $\sim 10^{13}$ /cm²/s) for 7 days in the Dhruva reactor, Mumbai, India to produce the ¹⁸¹Hf probe used for present measurements.

The TDPAC technique is based on substituting a trace amount of radioactive isotope into a well-defined chemical environment in a crystal [10]. Due to interaction of local EFG generated at the nuclear site with the nuclear quadrupole moment of the probe nucleus, the γ - γ angular correlation is perturbed. For electric quadrupole interaction in a polycrystalline sample, the perturbation function $G_2(t)$ for angular momentum $I=5/2$ \hbar of the intermediate level can be written as [11]

$$G_2(t) = S_{20}(\eta) + \sum_{i=1}^3 S_{2i}(\eta) \cos(\omega_i t) \exp(-\delta \omega_i t) \exp\left[\frac{-(\omega_i \tau_R)^2}{2}\right]. \quad (1)$$

The β^- decay of ¹⁸¹Hf populates the 615 keV level of ¹⁸¹Ta which is depopulated by emitting two successive γ -rays, 133 and 482 keV passing through the intermediate 482 keV $5/2^+$ level [12]. The angular correlation of the 133–482 keV γ - γ cascade is perturbed due to interaction of the nuclear quadrupole moment of the 482 keV level ($Q=2.35b$ [13]) with the electric field gradient generated at the nuclear site by the surrounding charge

distribution of the probe atom. The frequencies ω_i corresponding to transitions between the sublevels of the intermediate state arise due to nuclear quadrupole interaction (NQI). The parameter δ is the frequency distribution width and τ_R is the time resolution of the coincidence setup.

If more than one interaction frequencies are present in a sample due to the existence of either various non-equivalent sites within the same compound or due to mixture of different compounds, the perturbation function is given by

$$G_2(t) = \sum_i f_i G_2^i(t), \quad (2)$$

where f_i is the site fraction of the i th component. A fitting to the above expression for $G_2(t)$ determines the maximum component V_{zz} of the electric field gradient through the relation

$$\omega_Q = \frac{eQV_{zz}}{4I(2I-1)\hbar} \quad (3)$$

where the interaction frequencies ω_i are related to the quadrupole frequency ω_Q by $\omega_1=6\omega_Q$, $\omega_2=12\omega_Q$ and $\omega_3=18\omega_Q$ for the asymmetry parameter $\eta=0$. Here, Q is the nuclear quadrupole moment and I is the spin angular momentum of the intermediate level. The asymmetry parameter is defined as

$$\eta = \frac{(V_{xx} - V_{yy})}{V_{zz}} \quad (4)$$

and its value lies between 0 and 1. The values of ω_Q and η are generally used to describe the electric field gradient.

The TDPAC spectrometers used for present measurements consist of either a four detector BaF₂-BaF₂(50.8 × 50.8 mm²) or a four detector LaBr₃(Ce)-BaF₂ set up. For the LaBr₃(Ce)-BaF₂ set up, the LaBr₃(Ce) scintillators (38 × 25 mm²) used were procured from M/S Saint Gobain. The 133 keV γ -rays are selected in the LaBr₃(Ce) detectors and for this set up, a better time resolution is obtained compared to the BaF₂-BaF₂ set up. Standard slow-fast coincidence assemblies are used for both set up. Typical prompt time resolutions (FWHM) of ~ 1 ns and 700 ps have been obtained for the BaF₂-BaF₂ and LaBr₃(Ce)-BaF₂ set up, respectively, for the selected γ -ray energies of ¹⁸¹Ta. The ratio of coincidence counts at 180° and 90° for the time channel 't' is given by

$$R(t) = \frac{2}{3} \left[\sqrt{\frac{W_{13}(180^\circ, t)W_{24}(180^\circ, t)}{W_{14}(90^\circ, t)W_{23}(90^\circ, t)}} - 1 \right], \quad (5)$$

where $W_{ij}(\theta, t)$ are random subtracted coincidence counts for the coincidence combination of detectors i and j set at an angle θ . Details on the experimental set up and data acquisition have been described in our earlier report [14].

3. Results and discussion

3.1. HfF₄·3H₂O

The TDPAC measurement in the dried sample of Hf metal in concentrated HF at room temperature is carried out to look into the crystallized components. The PAC spectrum at room temperature (Fig. 1) shows an almost undamped periodic structure up to 50 ns which indicates a good crystalline nature of the sample. A fitting to the spectrum gives two quadrupole interaction frequency components (Table 1). The dominant component ($\sim 80\%$) produces values of quadrupole frequency $\omega_Q = 183.2(2)$ Mrad/s, asymmetry parameter $\eta=0.843(2)$ with a frequency distribution width $\delta=0.9$ (1)%. For the minor component ($\sim 20\%$), the values are found to be $\omega_Q = 203.7(8)$ Mrad/s, $\eta=0.377(8)$ and $\delta=1.0(4)\%$. The values found for the minor component can be compared with the

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