TDPAC study in ZnTiF₆·6H₂O between room temperature and 1273 K

M.A. Taylor, M. Ceolin and J.A. Martínez
Departamento de Física, Facultad de Ciencias Exactas,
Universidad Nacional de La Plata, CC67, 1900 La Plata, Argentina

Received 9 February 1994

Using the time differential perturbed angular correlation technique, the hyperfine interactions as titanium sites in ZnTiF₆·6H₂O and its decomposition products were determined between room temperature (300 K) and 1273 K. The different steps in the decomposition pattern were identified and a simple model is given for it.

1. Introduction

ZnTiF₆·6H₂O belongs to the class of compounds having the general formula A⁺⁺B⁴⁺F₆·6H₂O (A⁺⁺ = Mg, Mn, Fe, Co, Ni, Zn; B⁴⁺ = Ti, Zr, Si, Hf). These compounds have closely related crystal structures and consist of an arrangement of divalent ions [A⁺⁺(H₂O)₆]²⁺ and [B⁴⁺F₆]²⁻ octahedra. The octahedra are packed in a rhombohedral distorted CsCl-type structure [1].

Among the compounds of this family, exhaustive studies have been made on fluorosilicate and fluortitanate systems below room temperature using NMR, Raman spectroscopy, etc. [2–3]. On the other hand, very few members have been studied above room temperature [4].

In this paper the time differential perturbed angular correlation (TDPAC) study of ZnTiF₆·6H₂O between 300 and 1273 K is reported in order to investigate, from a microscopic point of view, the thermal decomposition of the compound.

2. Experimental

ZnTiF₆·6H₂O was prepared by dissolving ZnCO₃ in Hf doped fluortitanic acid. Once the compound was identified by X-ray analysis, the sample to be investigated was encapsulated in quartz tubes of 5 mm diameter at atmospheric pressure.
$^{181}\text{Hf}$ activity produced by thermal neutron irradiation of the compound populates the efficient 133–482 keV $\gamma-\gamma$ cascade of $^{181}\text{Ta}$ used in this investigation as TDPAC probe.

A two CsF detectors high time-resolution setup ($2\tau = 0.75$ ns at Ta energies) supplied with an electric furnace, which permitted to heat the sample in situ within ±1 K, was used to obtain the experimental results.

The hyperfine quadrupole parameters corresponding to each interaction, i.e. the quadrupole frequency $\omega = eQV_{zz}/4I(2I + 1)\hbar$, the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, the frequency distribution width $\delta$ and also the relative fractions $f_i$ of probe nuclei acted upon by different quadrupole interactions were obtained at different temperatures from the $A_{22}G_{22}(t)$ experimental curves (the so-called spin rotation curves). Details about the technique and the physical background are given elsewhere [5].

3. Results and discussion

Fig. 1 shows the TDPAC spectra of ZnTiF$_6$·6H$_2$O at selected temperatures. At room temperature the spin rotation curve was fitted with a single interaction whose quadrupole parameters are listed in table 1. The low frequency distribution width and the similarity with already determined hyperfine interactions in similar ABF$_6$·6H$_2$O compounds, indicated that the hafnium probes were clearly placed at crystallographic titanium sites. From fig. 2 it is possible to see that the quadrupole interaction frequency determined for tantalum nuclei in ZnTiF$_6$·6H$_2$O monotonically decreases on rising temperature. As it was already reported in ref. [6], this behavior can be explained assuming two different contributions to the thermal variation of the electric field gradient (EFG), one arising from the low frequency roto-vibrational modes of the structure (Bayer-Kushida model) and another originated in the dynamics of the hydrogen bond network ("flip" model, ref. [6] and references therein). Then the thermal evolution of the quadrupole interaction frequency can be written as

$$\omega_Q(T) = \omega_0 \left[ 1 - \frac{3}{8\pi^2} \left( \frac{h}{\theta_3\nu_3} \left[ \frac{1}{2} + \left( e^{\theta_3/kT} - 1 \right)^{-1} \right] \right) + \omega_0' \frac{1 + Re^{-E_0/kT}}{1 + e^{-E_0/kT}} \right],$$

where $\omega_0$ and $\omega_0'$ are the $T = 0$ quadrupole frequencies arising from the Bayer-Kushida model and the "flip" model respectively, $\theta_i$ and $\nu_i$ are the inertia constants and frequencies of the rotations around the C$_3$ and C$_4$ octahedral axis respectively, $E_0$ is the value of the gap in the two-level "flip" model and $R$ is the ratio of the EFG strengths associated to the upper and lower level of the "flip" model (for a more detailed discussion, see ref. [6]). Using eq. (3) and the values