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# Temperature dependence of the Ti-site electric-field gradient in titanite, $CaTiSiO_5$

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Using perturbed-angular-correlation (PAC) spectroscopy, we have measured nuclear-electric-quadrupole interactions at the Ti sites in ceramic samples of titanite that were doped with the $^{181}Hf \rightarrow ^{181}Ta$ PAC probe. Measurements were made over a temperature range from 10 to 980 K to investigate the effects of the antiferroelectric-to-paraelectric transition at approximately 500 K on the electric-field gradients (EFG's) at the Ti site. Near the transition temperature $T_c$, the magnitude $V_{zz}$ of the EFG shows no significant inflections. Over the entire temperature range, $V_{zz}$ decreases approximately linearly with increasing temperature, whereas $\eta$ remains relatively constant. The line-shape parameter $\delta$ decreases slowly with increasing temperature from 10 K to approximately $T_c$; at temperatures above $T_c$, $\delta$ remains relatively constant. Using a point-charge model, we attribute the absence of any discernible effects of the transition on the measured values of $V_{zz}$ and $\eta$ to the direction and symmetry of the Ti-ion displacement relative to the Ti-site EFG axes.

During the past two decades, several mineralogists have investigated a subtle phase transition in the naturally occurring mineral titanite $CaTiSiO_5$.[1–4] Speer and Gibbs[1] refined the laboratory-temperature structure, which Zachariasen[5] reported in 1930. They described this phase as being antiferroelectric, in which the Ti ions were displaced away from the centers of oxygen octahedra. Taylor and Brown[2] extended the investigation to elevated temperatures, and they characterized a reversible, displacive phase transition that occurred at approximately 500 K, in which the corresponding space group changed from $P2_1/a$ below the transition to $A2/a$ above $T_c$. Recently, Ghose, Ito, and Hatch[3] developed an order-parameter treatment of this antiferroelectric-to-paraelectric transition, which they based on high-temperature x-ray diffraction measurements, and Van Heurck *et al.*[4] used electron microscopy and electron diffraction to observe dynamical fluctuations at temperatures near $T_c$. Figure 1 shows the titanite structure schematically.

Perturbed-angular-correlation (PAC) spectroscopy uses the nuclear-electric-quadrupole moments of radioactive probe atoms to measure the extranuclear electric-field gradient (EFG) at specific lattice sites where the probes are substituted. The antiferroelectric-to-paraelectric transition in titanite involves primarily the displacement of the Ti ion from the center of its oxygen octahedron.[1–4] Also it is well known that $Hf^{4+}$ ions, which carry the $^{181}Hf$ radioactivity, can substitute for $Ti^{4+}$ ions in several ternary-metal-oxide ceramics.[6,7] For these reasons, the PAC measurement using the $^{181}Hf \rightarrow ^{181}Ta$ probe should be a good choice with which to investigate the local environment in the vicinity of the Ti site in titanite. Moreover, diffraction techniques, used in the earlier investigations,[1–4] primarily measure extended structural features. The diffraction-derived structures represent spatial averages over the details of the entire crystal, whereas the PAC technique via the nuclear-electric-quadrupole interaction measures the local probe environment. Hence, the PAC measurements sometimes reveal structural nuances that involve long-range interactions associated with phase transitions, because the local EFG's may cou-

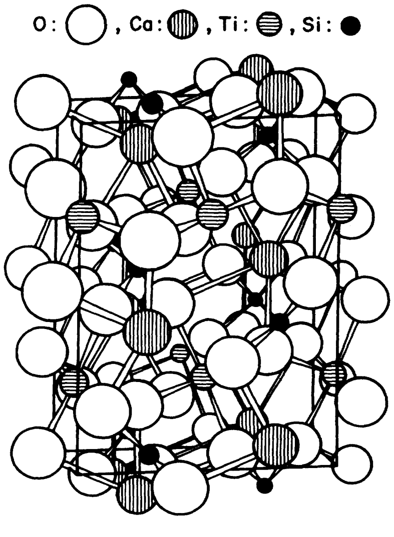

FIG. 1. Structural diagram of titanite.

ple to the order parameter of the transition. Recently, we reported two different examples of ferroic ternary metal oxides that illustrate this effect.[8,9] We thus decided to use the $^{181}\mathrm{Hf}\rightarrow{}^{181}\mathrm{Ta}$ PAC probe to measure the EFG temperature dependence at the Ti site in ceramic titanite. The questions that we address are (1) Can the $^{181}\mathrm{Hf}\rightarrow{}^{181}\mathrm{Ta}$ probe be substituted into the Ti site, and can well-defined static interactions be measured that yield unique EFG parameters? (2) If so, does the EFG temperature dependence reveal any additional information about the antiferroelectric-to-paraelectric transition?

Ceramic samples of $\mathrm{CaTiSiO_5}$, which were doped with either 0.5 or 2 at. % Hf that carried the $^{181}\mathrm{Hf}$ radioactivity, were prepared using a resin-intermediate method. The metal-ion precursors, $\mathrm{CaCO_3}$, $\mathrm{Si(O_2C_2H_3)_4}$, and $\mathrm{Ti(OC_3H_7)_4}$, were added to a solution of ethylene glycol and citric acid. Upon heating, the solution formed a polyester resin that was subsequently pyrolyzed. The pyrolyzed resin was calcined at 1070 K, and the resulting powder was pressed into sample pellets and sintered at 1400–1500 K for several hours. Subsequent x-ray-powder-diffraction patterns indicated that the radioactive sintered-pellet samples were phase pure.

The PAC measurements were made at the Pennsylvania State University (PSU) using a four (CsF) -detector apparatus[10] and at the University of Maryland Baltimore County (UMBC), using a three (one CsF and two $\mathrm{BaF_2}$) -detector apparatus. The cryogenic-temperature measurements were made using a Displex closed-loop refrigerator, and the elevated-temperature measurements were made using a resistance-wire-wrapped ceramic tube furnace. A one-site model for static nuclear-electric-quadrupole interactions in a polycrystalline source was sufficient to analyze the measured perturbation functions:

$$-A_{22}G_{22}(t_i)=A_1\left[S_0(\eta)+\sum_{k=1}^{3}S_k(\eta)\exp(-\tfrac{1}{2}\delta\omega_k t_i)\cos(\omega_k t_i)\right]+A_2\ . \qquad (1)$$

Here, $A_1$ is the normalization factor, $\delta$ is the line-shape parameter, and $A_2$ takes into account the effects of $\gamma$ rays that are absorbed by the sample en route to the detectors and to some extent the fraction of probe atoms that are not in a well-defined chemical environment. The frequencies $\omega_k$ and the $S_i(\eta)$ coefficients describe a static interaction in a polycrystalline source. Using nonlinear regression, the free parameters $\omega_1$, $\omega_2$, $A_1$, $A_2$, and $\delta$ were derived from each data set, in which the experimental time resolution, $\approx 1$ nsec (PSU) and $\approx 0.7$ nsec (UMBC) full-width-at-half-maximum, was taken into account. The ratio $\omega_2/\omega_1$ was used to determine the quadrupole frequency $\omega_Q$, which is $\omega_1/6$ when $\eta=0$.[10] The nonvanishing EFG components $V_{ii}$ in the principal-axis system where the probe nucleus is at the origin are related to the quadrupole frequency $\omega_Q$, and the asymmetry parameter $\eta$ by $\omega_Q=[eQV_{zz}/4I(2I-1)\hbar]$ and $\eta=(V_{xx}-V_{yy})/V_{zz}$, in which $Q$ is the nuclear quadrupole moment (2.51 b) and $I$ is the nuclear spin ($\frac{5}{2}$).

Figure 2 presents the perturbation functions measured on a 2 at. % Hf-doped $\mathrm{CaTiSio_5}$ ceramic sample and the fitted curves. Figure 3 summarizes the derived parameters $V_{zz}$, $\eta$, and $\delta$ for two titanite samples, one doped with 2 at. % Hf and one doped with 0.5 at. % Hf. From the other derived parameters $A_1$ and $A_2$, site occupancy fractions $f_1=A_1/(A_1+A_2)$, which showed no temperature variations, were determined, $f_1=98\pm1$ and $97\pm2$ %, for the two samples.

The interaction frequencies $\omega_K$ are very high, perhaps they are the highest frequencies reported for $^{181}\mathrm{Hf}\rightarrow{}^{181}\mathrm{Ta}$ PAC measurements on ternary metal oxides. For this reason, the measured perturbation functions show mainly the effects of the lowest-frequency $\omega_1$. The components that contain $\omega_2$ and $\omega_3$ are attenuated by the finite time resolution of the spectrometer. As a result, the fitting procedure cannot distinguish unambiguously between interaction frequencies that represent $\eta$ values near zero and those near unity. During the fitting procedure, we obtained fits that converged near small $\eta$ values and large $\eta$ values. The associated $\chi^2$ values and visual inspection indicate that the small $\eta$ values represented the better fits. Additionally, the low-asymmetry-parameter fits are consistent with the crystallographic symmetry of the Ti site. Measurements on a single-crystal sample could remove this ambiguity. The amplitudes of the frequency components could be varied by orienting the crystal axes in different directions to determine $\eta$. But, unfortunately, titanite single crystals doped with $^{181}\mathrm{Hf}$ were not available.

The perturbation functions shown in Fig. 2 and the derived parameters indicate that the $^{181}\mathrm{Hf}\rightarrow{}^{181}\mathrm{Ta}$ probes undergo a single, static interaction in a well-defined chemical environment. The ionic radii of the $\mathrm{Ti^{4+}}$ and $\mathrm{Hf^{4+}}$ ions are 0.745 and 0.85 Å, respectively, for octahedral coordination.[11] This similarity and the similarity in the ionic charges suggest strongly that $^{181}\mathrm{Hf}\rightarrow{}^{181}\mathrm{Ta}$ probes substituted into the Ti sites in $\mathrm{CaTiSiO_5}$. In addition, the Ca site is a large, irregular cavity that has seven coordination,[1] and the Si site is relatively small and has tetrahedral coordination.[1] Thus by observing a single well-defined interaction with low asymmetry and by considering this crystal-chemical information, we can assign, self-consistently, the probe substitution to the Ti site.

Although the chemistry of the $\mathrm{Hf^{4+}}$ ion determines where the probe substitutes, the $^{181}\mathrm{Ta}$ excited nucleus interacts with the extranuclear environment at the probe site. The $\beta^-$ decay of the $^{181}\mathrm{Hf}$ nucleus primarily populates the $I=\frac{1}{2}$ excited level at 615 keV in $^{181}\mathrm{Ta}$ that has a half-life of 18 $\mu$s. Thus the chemistry of the $^{181}\mathrm{Ta}$ probe should be that of an electronically equilibrated $\mathrm{Ta^{5+}}$ ion at a Ti site. As a result, the absolute magnitudes of the measured, local EFGs may differ from those experienced by the indigenous Ti nuclei. However, the relative values of the measured EFG temperature dependence should reflect the actual effects of the phase transition.

As seen in Fig. 3, the EFG component $V_{zz}$ shows a decrease with increasing temperature that a linear fit represents reasonably well. The asymmetry parameter $\eta$ does not change significantly over the temperature range. More important, neither of these quantities show either an inflection or a discontinuity at temperatures near $T_c$ ($\approx$500 K). Therefore, the effects of the antiferroelectric-to-paraelectric transition are conspicuous by their absence. The line-shape parameter $\delta$ shows a slow decrease with increasing temperature from 10 K to approximately $T_c$; and above $T_c$, $\delta$ remains relatively constant. This effect suggests that, at temperatures well below $T_c$, collective motion such as the twisting of the Ti octahedra could give rise to a slowly time-varying interaction that produces some line broadening via nuclear-spin relaxation. At higher temperatures, the rate of this motion may increase and cause motional narrowing that diminishes the line broadening.

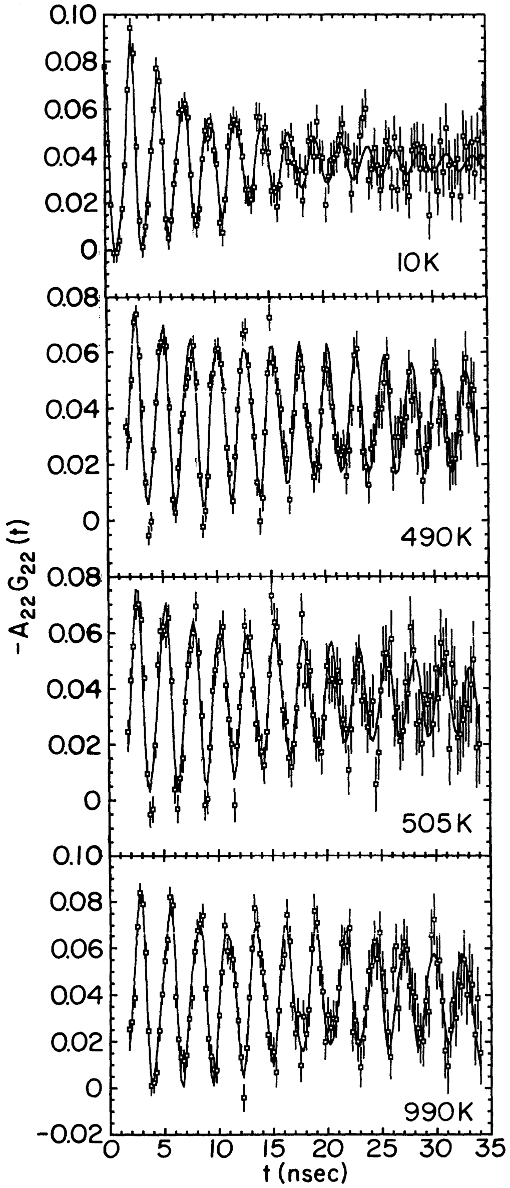

FIG. 2. Perturbation functions for a $CaTiSiO_5$ ceramic sample that was measured at the indicated temperatures. The solid lines represent fits of Eq. (1) to the data. In the perturbation function measured at 10 K, the increased line broadening is evident.

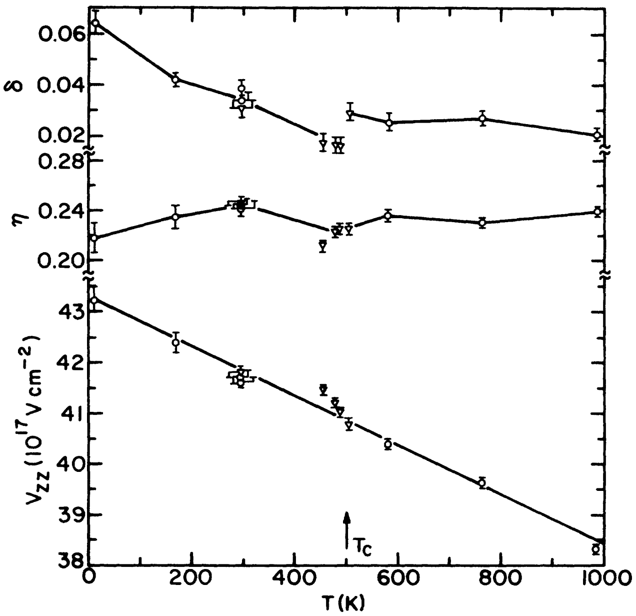

FIG. 3. Electric-field-gradient parameters $V_{zz}$ and $\eta$ and the line-shape parameter $\delta$. The circles and the triangle indicate values for a $CaTiSiO_5$ sample doped with 2 and 0.5 at. % Hf, respectively. The line through the $V_{zz}$ data points represents a least-squares fit that gives a slope = $(4.8\pm0.4)\times10^{14}$ V $cm^{-2}$ $K^{-1}$ and an intercept $=(43.3\pm0.5)\times10^{17}$ V $cm^{-2}$. The other lines are shown to guide the eye. The phase transition temperature occurs at approximately 500 K.

To understand the absence of any apparent effects of the phase transition on the measured static EFG's, we consider some details of the titanite structure in the contest of the point-charge model. In this simple model, the EFG components are calculated by representing the crystal as an array of point charges. We further assume that the nearest-neighbor O ions, i.e., the oxygen octahedron, make the most significant contribution to the Ti-site EFG. This assumption is justified because the titanium-oxygen octahedron is enormously distorted along the direction of the fourfold rotation axis and generates a huge EFG. Then the model for $N$ ions is given by

$$V_{ij}=e(1-\gamma_\infty)\sum_{k=1}^{N} q_k[3(x_i x_i)_k-\delta_{ij}r_k^2]/r_k^5\ , \qquad (2)$$

in which $q_k$ is the charge on the $k$th ion and $x_i$ $(i=1,2,3)$ are the Cartesian coordinates of the $k$th ion. The antishielding factor is $(1-\gamma_\infty)$, which is taken as 62.[12] Using structural data for 438 and 543 K,[2] the calculation gives $V_{zz}=-2.2\times10^{18}$ $V\,cm^{-2}$ and $\eta=0.26$, and

$V_{zz}=-2.2\times10^{18}$ V cm$^{-2}$ and $\eta=0.24$, respectively. In this temperature range, the experimental values of $V_{zz}$ are approximately twice as large and $\eta\approx0.22$. The absolute values of $V_{zz}$ that the model gives for ionic crystals may differ by large amounts, such as by a factor of 2, from the experimental values, because the values of the antishielding factors are not well known and because the model does not account for any details of covalent bonding. For the same reasons, model values of $\eta$ may be inaccurate also. But the relative values of $V_{zz}$ and $\eta$, which are calculated for a particular structure for several different temperatures, for example, should be more reliable.[13,14] In this case, the model values of $V_{zz}$ and $\eta$ show either no or very little temperature sensitivity. Although the experimental values of $V_{zz}$ decrease slowly with increasing temperature, neither the model nor the experiment shows any effects of the phase transition. This decrease in the experimental values of $V_{zz}$ can be attributed to the effects of anisotropic vibrational modes.[14]

The insensitivity of the model to the effects of the phase transition as well as to the effects of temperature can be explained by considering the lengths of the Ti-O bonds that form the oxygen octahedron. Over the temperature range from 294 to 700 K, the four Ti-O bonds that lie near or in the plane perpendicular to the fourfold rotation axis of the oxygen octahedron vary less than $\approx0.01$ Å in length.[3] For our purposes, these bond lengths may be considered as constant over this temperature range. However, the two Ti-O bonds that form the apices (parallel to the fourfold rotation axis) of the octahedron have lengths, 1.770(3) and 1.983(3) Å, at 294 K, and lengths, 1.876(1) and 1.876(1) Å, at 700 K.[3] In the point-charge approximation, the contribution of the apical O ions to $V_{zz}$ is proportional to the sum of the two inverse-apical-bond lengths cubed, $r_1^{-3}+r_2^{-3}$, which is 0.3086 Å$^{-3}$ at 294 K and 0.3029 Å$^{-3}$ at 700 K. Moreover, the apical bond lengths are much shorter than the planar bond lengths. This difference creates a large distortion of the oxygen octahedron and gives rise to the enormous EFG at the Ti site, and the large difference between the lengths of the two apical Ti-O bonds at low temperatures produces the dipole moments associated with the antiferroelectric phase. But in the point charge sum when the lengths of both apical Ti-O bonds are approximately the same, the total contribution to $V_{zz}$ of the terms that represent the apical O ions is insensitive to whether either one Ti-O bond is short and the other is long or both bonds are the same length. Thus, over this temperature range, because the planar bond lengths remain constant and the apical bond lengths sum to approximately the same total length, the Ti-site EFG is not sensitive to the effects of the antiferroelectric-to-paraelectric transition.

In conclusion, the $^{181}\mathrm{Hf}\rightarrow{}^{181}\mathrm{Ta}$ PAC probe can be used to measure well-defined, static nuclear-electric-quadrupole interactions at the Ti site in ceramic titanite. Neither the EFG magnitude $V_{zz}$ nor the asymmetry parameter $\eta$ give any additional information about the antiferroelectric-to-paraelectric transition, although the temperature dependence of the line-shape parameter $\delta$ does indicate that a relaxation mechanism may be operative. Interestingly, the displacement of the Ti ion away from its crystallographic site, which characterizes the antiferroelectric phase, occurs nearly along the $z$ axis of the EFG (in the principal-axis system). The symmetry of this displacement causes the EFG to remain relatively constant over the temperature range near $T_c$.

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