Structural Phase Transitions in BaTiO₃ Studied via Perturbed Angular Correlations

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Phase transitions in the ferroelectric perovskite BaTiO₃ were studied for ¹¹¹In-implanted polycrystalline samples by measuring the electric field gradients by means of Perturbed Angular Correlation spectroscopy. The phase transitions between the orthorhombic ↔ rhombohedral ↔ tetragonal ↔ cubic lattices were investigated in ± 10 K steps, for increasing and decreasing temperatures, in order to determine their hysteresis. The transition parameters are compared with results from measurements of the spontaneous polarization, electric susceptibility and neutron scattering.

Key words: Perturbed Angular Correlations; BaTiO₃; Phase Transitions; Hysteresis; ¹¹¹In.

1. Introduction

Among the perovskites, BaTiO₃ is the most important ferroelectric compound which is widely used in electromechanical actuators, sensors, ceramic capacitors and photo-galvanic devices [1-3]. Its electric susceptibility, etc. Previous results from Perturbed Angular Correlation (PAC) spectroscopy in BaTiO₃, Ba(TiHf)O₃, and CdTiO₃ using ¹⁸¹Hf/¹⁸⁰Ta probes have been reported by Catchen et al. [4 - 6] and by Schäfer et al. [7]. Recently, Uhrmacher and collaborators [8] have published first PAC results in BaTiO₃ using ¹¹¹In/¹¹¹Cd hyperfine probes. Their survey measurements showed the occurrence of electric field gradients (EFG) in the non-cubic phases, present below the Curie temperature $T_C = 393$ K. Structural phase transitions can be monitored via PAC, if the hyperfine probe atoms substitute specific cation lattice sites. Several recent studies on perovskites of the type $A_2B^{4+}O_3$ [9, 10] using ¹⁸¹Hf and ¹¹¹In probe nuclei have given evidence that the main hyperfine fraction can be attributed to substitutional B-site implantation of the probes.

The present PAC measurements for ¹¹¹In/¹¹¹Cd probes in polycrystalline BaTiO₃ samples aim at scanning, in finer temperature steps than in [8], the structural phase transitions, which occur between the cubic phase (I, paraelectric), the tetragonal phase (II), the orthorhombic phase (III), and the rhombohedral phase (IV). The approximate transition temperatures are $T_0 = 193$ K for the IV ↔ III transition, $T_0' = 278$ K for the III ↔ II transition and $T_C = 393$ K for the II ↔ I transition [4 - 6, 8].

2. Experiments

The PAC measurements were carried out for polycrystalline BaTiO₃ powder samples of 99.995% purity which were pressed into pellets, 4 mm in diameter and 0.5 mm thick. Powder X-ray diffraction analyses at room temperature revealed that all observed reflexes could be assigned to the expected tetragonal phase. Some 10¹²¹¹In+ ions were implanted at 400 keV ion energy into the samples, using the Göttingen ion implanter IONAS [11]; the implantation depth was about 60 nm. After implantation the samples were annealed for four hours at 1673 K in air in order to remove radiation damage. For the measuring temperatures below 300 K, the samples were mounted at the pole tip of either a closed-cycle helium cryostate ($T = 10 - 230$ K) or a Peltier element ($T = 275 - 296$ K). Both cryostates were housed in vacuum chambers at pressures of 10⁻⁶ - 10⁻⁵ mbar. Measurements above room temperature...
were carried out under air in an oven of low \( \gamma \)-ray absorption. We estimate that the given temperatures are correct within better than \( \pm 0.4 \) K.

The PAC spectra were accumulated using a set-up of four NaI(Tl) detectors in 90° geometry. The perturbation functions \( R(t) \) were fitted by assuming, at each temperature, two fractions \( f_t \) and \( f_k = 1 - f_t \), which are characterized by their respective static EFG parameters [12], i.e. the quadrupole frequency \( \nu_0 \), asymmetry parameter \( \eta \) and frequency width \( \delta \). Figure 1 illustrates the evolution of the perturbation function \( R(t) \) and its Fourier transform \( F(\omega) \) across the III \( \Rightarrow \) II phase transition, where the temperature was increased from 281 K to 295 K. Evidently, as shown in Fig. 2, the hysteresis of this phase transition shows up via the temperature dependences of the two competing fractions \( f_{\text{III}}^{1/1} \) and \( f_{\text{II}}^{1/1} = 1 - f_{\text{III}}^{1/1} \), for increasing or decreasing temperature. Finally, Fig. 3 displays the II \( \Rightarrow \) I phase transition which occurs very suddenly.

3. Electric Field Gradients and Site Occupation

The deduced EFG parameters for \(^{111}\)Cd (and for \(^{181}\)Ta [4 - 6]) measured in the various phases of BaTiO\(_3\) are listed in Table 1. In the case of the \(^{111}\)Cd probes, one notes symmetric EFG's in the phases II and IV (\( \eta_{\text{IV}} = \eta_{\text{II}} = 0 \)), while the EFG of the phase
Table 1. Electric field gradients of $^{111}\text{Cd}$ and $^{181}\text{Ta}$ probes in BaTiO$_3$.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$T$ (K)</th>
<th>$\nu_Q$ (MHz)</th>
<th>$\eta$</th>
<th>$\delta$</th>
<th>$T$ (K)</th>
<th>$\nu_Q$ (MHz)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV, rhombohedral</td>
<td>80</td>
<td>6.3(24)</td>
<td>3.1(16)</td>
<td>80</td>
<td>63(17)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>III, orthorhombic</td>
<td>227</td>
<td>22.0(8)</td>
<td>0.37(6)</td>
<td>1.1(6)</td>
<td>220</td>
<td>137(12)</td>
<td>0.4(1)</td>
</tr>
<tr>
<td>II, tetragonal</td>
<td>293</td>
<td>33.3(7)</td>
<td>0</td>
<td>1.4(5)</td>
<td>293</td>
<td>205(12)</td>
<td>0</td>
</tr>
<tr>
<td>I, cubic</td>
<td>475</td>
<td>0</td>
<td>0</td>
<td>43(10)</td>
<td>400</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

III is asymmetric, $\eta_{III} = 0.37(6)$. All EFG's are well defined, with the width parameters being only $\delta = 1 - 3$ MHz. When comparing the EFG parameters for $^{111}\text{Cd}$ and $^{181}\text{Ta}$ probes, we note that the asymmetry parameters $\eta$ agree fairly well for the various phases. Furthermore, the ratios of the quadrupole frequencies $\nu_Q$ for both probes agree with the ratio $\nu_Q^{(181}\text{Ta})/\nu_Q^{(111}\text{Cd}) = 6.5(10)$ predicted by the point charge model for the B-site, if we infer the appropriate quadrupole moments and Sternheimer factors of the two probe nuclei. This agreement of asymmetry parameters and frequency ratios thus strongly supports that both types of probe ions are being implanted into the B-site and substitute Ti. This conclusion is supported by PAC measurements with $^{181}\text{Hf}/^{181}\text{Ta}$ probes in SrHfO$_3$ and BaHfO$_3$ perovskites, following...
neutron activation of $^{180}$Hf [9], and in our previous paper on $^{111}$In/$^{111}$Cd in BaTiO$_3$ [8]. Similar results have also been discussed by Luthin et al. [13] for $^{111}$Cd in ZrO$_2$ and HfO$_2$ and by Wiarda et al. [14] for a large number of other binary oxides.

4. Phase Transition Parameters

Let us now discuss, for the three phase transitions in BaTiO$_3$ considered, the temperature dependence of the fractions $f_1^1$ that reveal the hysteresis. As usual, we introduce the transition temperatures $T_0^1$ and $T_0^1$, at which the two competing fractions are equal when increasing or decreasing the temperature across a phase transition. The quantity $\delta T_0 \equiv |T_0^1 - T_0^1|$ measures the width of the hysteresis. The “smoothness” of a phase transition can be expressed by the quantities $\Delta T^1$ and $\Delta T^1$, where we used the approximation

$$f_1^1(T) = \{1 \pm \exp[(T - T_0^1/\Delta T^1/1)]\}^{-1}$$

for that fraction which has disappeared well above the transition temperature $T_0^1/1$. In Table 2, the deduced transition parameters are compared with the values reported from neutron diffraction, electric susceptibility and polarization experiments [1, 15, 16]. Only in the case of the III $\rightarrow$ II transitions, we have obtained precise values of $T_0^1/1$ and $\Delta T^1/1 = 1.7(2)$ K.

We first notice that the widths parameter $\delta T_0$ generally decreases for increasing transition temperatures, i.e. $\delta T_0^{IV \rightarrow III} \approx 7.5 - 25$ K, $\delta T_0^{III \rightarrow II} = 6$ K, and $\delta T_0^{II \rightarrow I} < 2$ K. Furthermore, the transition temperatures $T_0^1/1$ themselves measured with different methods do not agree with each other. A possible explanation has been given by Zhong et al. [17] who found that the annealing conditions of the samples determine the grain size and consequently the transition parameters. In this way, changes of $T_0^1/1$ by as much as 10 K have been observed, if the annealing temperature varies between 1273 K and 1423 K.

In conclusion, we have determined the electric field gradients of dilute $^{111}$Cd impurities in polycrystalline BaTiO$_3$ samples. For each of the known phase transitions, we have deduced the EFG parameters, the transition temperatures $T_0^1/1$ and, in the case of the orthorhombic $\Leftrightarrow$ tetragonal (III $\Leftrightarrow$ II) transition, the average smoothness parameter $\Delta T^1/1 = 1.7(2)$ K. In view of the different values of $T_0^1/1$ observed with various methods, PAC measurements in single-crystals are required in future experiments. Furthermore, the influence of an external electric field on the EFG parameters also appears to be an interesting extension of the present study.

Table 2. Transition parameters in BaTiO$_3$ as obtained with different methods.

<table>
<thead>
<tr>
<th>Transition $T_0^1$ (K)</th>
<th>$T_0^1$ (K)</th>
<th>$\delta T_0$ (K)</th>
<th>Method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV $\rightarrow$ III</td>
<td>202.5</td>
<td>195</td>
<td>7.5 PAC, $^{111}$Cd</td>
<td>Present work</td>
</tr>
<tr>
<td>IV $\rightarrow$ III</td>
<td>203</td>
<td>178</td>
<td>25 Polarization</td>
<td></td>
</tr>
<tr>
<td>IV $\rightarrow$ III</td>
<td>195</td>
<td>178</td>
<td>17 Susceptibility</td>
<td>[15]</td>
</tr>
<tr>
<td>III $\rightarrow$ II*</td>
<td>290.4</td>
<td>284.3(3)</td>
<td>6.1(3) PAC, $^{111}$Cd</td>
<td>Present work</td>
</tr>
<tr>
<td>III $\rightarrow$ II*</td>
<td>274</td>
<td>269</td>
<td>5 PAC, $^{181}$Ta</td>
<td>[7]</td>
</tr>
<tr>
<td>III $\rightarrow$ II*</td>
<td>284</td>
<td>278</td>
<td>6 Neutron diff.</td>
<td>[16]</td>
</tr>
<tr>
<td>III $\rightarrow$ II*</td>
<td>276</td>
<td>270</td>
<td>6 Polarization</td>
<td></td>
</tr>
<tr>
<td>III $\rightarrow$ II*</td>
<td>277</td>
<td>270</td>
<td>7 Susceptibility</td>
<td>[15]</td>
</tr>
<tr>
<td>II $\rightarrow$ I</td>
<td>389</td>
<td>389</td>
<td>&lt; 2 PAC, $^{111}$Cd</td>
<td>Present work</td>
</tr>
</tbody>
</table>

$^*$ $\Delta T^1 = 1.6(2)$ K; $\Delta T^1 = 1.8(3)$ K.


