**Phase transition hysteresis at the antiferroelectric-ferroelectric boundary in PZT**

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PbZr$_{1-x}$Ti$_x$O$_3$ exhibits an antiferroelectric (AFE)-ferroelectric (FE) phase boundary at the composition $x \sim 0.06$. At room temperature, compositions with $x < 0.06$ possess AFE $Pbam$ structure, and compositions with $x > 0.06$ possess FE $R3c$ structure. Upon heating, both phases transit into an intermediate (IM) state [1, 2]. Around this boundary, there are several questions in need to be answered, such as the stabilizations of different phases with a small amount of compositional difference, the sequence of phase transitions, crystal structures, and potential applications [3].

In this work, we have investigated PbZr$_{1-x}$Ti$_x$O$_3$ ($0.04 \leq x \leq 0.07$) single crystals and ceramics to reveal their local and average structures and the process of transformation with temperature. Optical experiments and x-ray and neutron scattering results show that, near the phase boundary, the AFE and FE structures coexist with a continuously changing ratio as a function of $x$. The complete phase diagram has been established. The AFE domains tend to be of smaller sizes with increasing $x$ and finally become a local-structural component upon entering the FE side. A peculiar transition path $Pbam \rightarrow$ IM state $\rightarrow$ $R3c \rightarrow Pbam$ has been discovered near the phase boundary. It is confirmed that $Pbam$ and $R3c$ structures maintain a subtle balance at the phase boundary, which may be perturbed by a slight change in the concentration or other external stimuli [4]. These findings provide new insights in understanding the antiferroelectric-ferroelectric competition and, hence, in designing new materials for energy storage and conversion.

![Figure 1](image-url)

**Figure 1.** X-ray diffuse scattering patterns on the $(h00)_{pc}$ plane during the phase transition of a single crystal with $x \sim 0.05$. The squares indicate typical quarter reflections, and the triangle indicates a typical $M$ point.