PANalytical Empyrean

APPLICATION NOTE | Determination of Phase Transition Temperature in Ferroelectrics

Ferroelectric materials are used in a wide variety of applications including capacitors, non-volatile memory, sensors, actuators and transducers. However, a ferroelectric material has a maximum application temperature where its ferroelectricity disappears as a result of ferroeletric to paraeletric phase transition. This temperature is called the Curie temperature (T_C). For example, a $PbZr_{1-x}Ti_xO_3$ (PZT) exhibits a paraelectric cubic phase at above its T_C and lower symmetry ferroelectric (tetragonal and/or rhombohedral) phases below T_C, as shown in figure 1.

There are several methods can be used to determine the phase transition temperature of a ferroelectric material, the common methods including dielectric properties measurements, differential scanning calorimetry (DSC), anelastic measurements and *in situ* X-ray diffraction. Phase transition temperature and structural evolution of a commercial PZT (EC65) ceramic was characterized using *in situ* X-ray diffraction (XRD) measurement in this study.

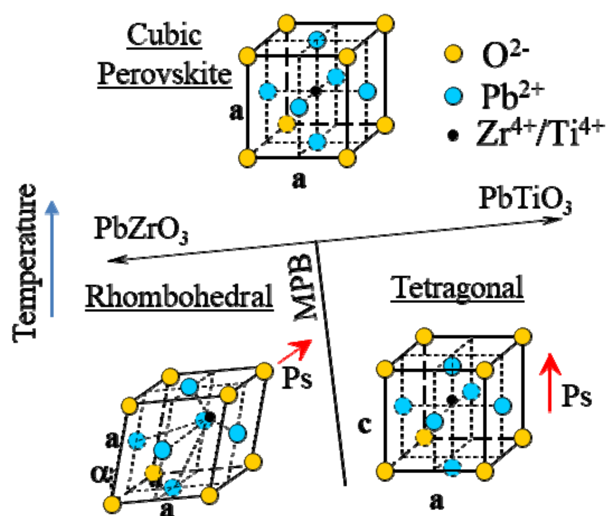

Figure 1. An illustration of conventional phase diagram of PZT.

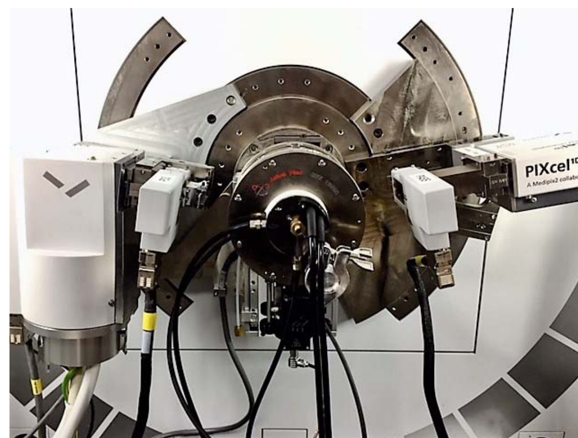

Figure 2. Front view of *in situ* X-ray diffraction setup with X-rays coming from the left, traveling through the HTK1200N furnace at the center of the figure, and diffraction signals were collected by an PIXel1D detector on the right.

Structural evolution as function of temperature of all compositions were investigated using a Panalytical Empyrean X-ray diffractometer with an Anton Parr HTK 1200N high temperature oven chamber. The *in situ* XRD setup is shown in figure 2. A 10 mm x 10 mm x 1 mm EC65 was heated in the chamber from 25 °C to 500 °C with a heating rate of 2°C/min. Each pattern was measured for 2 minutes using a step size and count time of 0.0263° 2θ and 52 sec/step, respectively. At room temperature, EC65 exhibits a tetragonal (P4mm) phase. And evolution of 002 and 200 diffraction peaks as a function of temperature was used to determine the ferroelectric to paraelectric phase transition temperature (i.e. Curie temperatue, T_C).

Figure 3 shows the temperature dependence of X-ray diffraction, dielectric properties, and mechanical stiffness of EC65. As seen in the top subplot of figure 3, 002 and 200 diffraction peaks were merging together with increasing temperature. Two 002 and 200 peaks of the tetragonal phase were eventually transition into one 200 peak of the cubic phase (Pm3m) in the elevated temperatures. The Curie temperature of EC65 is at 340 °C, which is determined by the temperature when 2 peaks first merged into 1 single peak.

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The phase transition temperature determined by *in situ* XRD measurement was valid by comparing to its temperature dependent dielectric properties and anelastic properties. Anelastic property measurements were conducted using a dynamic mechanical analyzer (Perkin-Elmer DMA 8000). Storage modulus (*E′*) and mechanical loss (*E′′/E′*) of each sample were acquired during heating with a heating rate of 2 °C/min and a vibration frequency range of 0.1 Hz to 10 Hz. Dielectric measurements were conducted in a temperature range of 25 °C to 500 °C with a heating rate of 2 °C/min. Dielectric properties of all compositions were determined from capacitance measurements using an Angilent 4282A LCR meter equipped with a NorECS ProboStat high temperature cell at Oregon State University.

Storage modulus *E′*, dielectric permittivity ε_r, and corresponding losses *E′′/E′* and tan δ were shown in the middle and bottom subplots in figure 3, respectively. An anomaly correlated to ferroelectric to paraelectric phase transition was clearly disguisable in *E′*, *E′′/E′*, ε_r, and tan δ when temperature approaching to its phase transition temperature. The phase transition temperatures determined by *in situ* XRD, dielectric, and anelastic measurements for all compositions were listed in table I. The difference in the phase transition temperatures determined by different measurements was less than 10 °C, which can be resulted from the instrumentation error. The results indicated that the phase transition temperature determined by *in situ* XRD measurement is consistence with other conventional testing methods, such as dielectric and anelastic measurement.

Table I Curie Temperature of EC65

Trade name	T_C^{XRD}(°C)	T_C^{D}(°C)	T_C^{A}(°C)
NOVA 3B	287	290	283
K270	308	312	314
K340	182	179	172
K350	372	361	366
EC65	338	341	345

T_C^{XRD}: Curie temperature determined by XRD

T_C^{D}: Curie temperature determined by dielectric measurements

T_C^{A}: Curie temperature determined by anelastic measurements

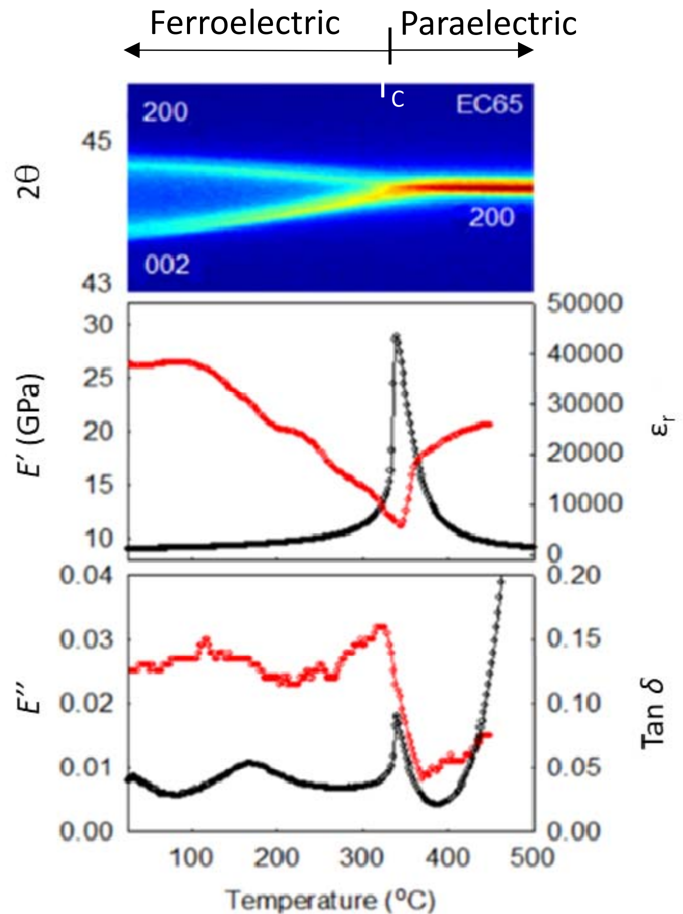

Figure 3. Temperature dependence of X-ray diffraction, dielectric properties, and mechanical stiffness of EC65. Dielectric permittivity (ε_r) and loss (Tan δ) were acquired at 1 kHz, and storage modulus (*E′*) and mechanical loss (*E′′/E′*) were acquired at 1Hz.

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