Polar Metastable States in Antiferroelectrics

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During the last few years antiferroelectricity has got a revival, due to its possibilities for energy storage thanks to the electrocaloric effect, and also for information storage because of the natural nano-domain structure of all antiferroelectrics. The prototypic antiferroelectric material is $PbZrO_3$, which on cooling undergoes a first order first transition from a cubic paraelectric phase to an orthorhombic antiferroelectric one with a huge multiplication of its unit cell. However, its antiferroelectric behavior is also in competition with a polar instability [1]; therefore, it is quite natural that $PbZrO_3$ becomes ferroelectric under electric field, pressure or a small ionic substitution. Small amounts of Ti induce an intermediate ferroelectric phase on cooling from the paraelectric phase, before the development of its antiferroelectric ground state [2], and in related antiferroelectrics, like $Pb(Zr,Sn)O_3$, more than one intermediate phase are present [3].

In this talk I will show the development of these intermediate ferroelectric phases and the metastable thermodynamic character they possess in two groups of samples:

In single crystals of $PbZrO_3$ substituted with 1% of Ti: samples were investigated by optical microscopy, and micro-Raman scattering, on heating to and cooling from its cubic phase. The visual recordings confirmed that these crystals undergo two phase transitions within the approximate temperature range 215–230°C (488–503 K). The way in which the intermediate phase develops across the crystal depends strongly on the defects present in the sample and on the heating/cooling velocity and prehistory of the crystals [2].

In antiferroelectric $Pb(Zr,Ti)O_3$ ceramics, with amounts of Ti up to about 10% [4,5]: Dielectric and anelastic experiments, as well as second harmonic generation and Raman scattering showed that there are intermediate polar states in these samples too, at lower temperatures, very dependent on the thermal prehistory of the samples when Ti amount is lower than 8%. The availability of these states near room temperature depends on the delicate thermal treatment of the sample and the heating and cooling rates.
Due to the presence of the second harmonic signal, the intermediate states are polar, at least partially, and probably ferroelectric. A good understanding of their behavior and control is the key to develop better energy storage devices based on antiferroelectrics.

References
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