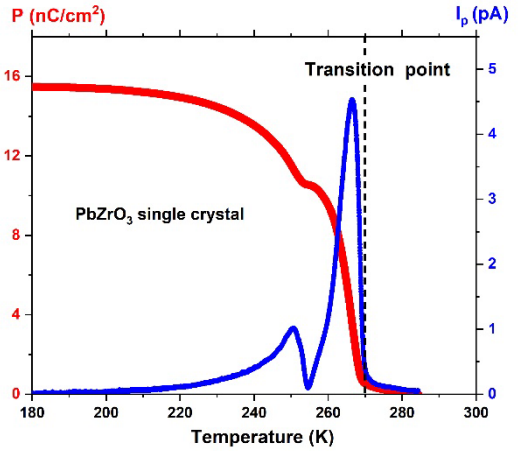
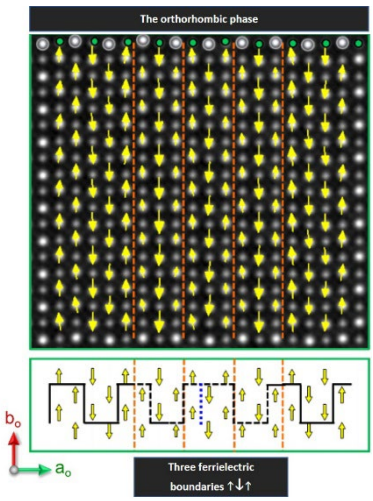
Unusual low-temperature polarity in the antiferroelectric perovskite crystals

Lead zirconate $PbZrO_3$, the first antiferroelectric material discovered in the history of ABO_3 perovskites, became the prototype (archetype) of the antiferroelectric compound. At first, it was only a scientific curiosity, but later it turned out to be an extremely interesting compound from the point of view of fundamental research. Although it has been studied for more than 70 years, it is only in the last ten years that discoveries have been made of its extremely interesting and unusual physical properties concerning its complicated - compared to ferroelectrics - phase transition mechanism, unconventional paraelectric phase with nano-polar areas, jerky domain wall motion, flexoelectric phenomenon, large negative electrocaloric effect, energy storage, cycloidal polarisation ordering and thermal conductivity switched in an electric field or laser light. $PbZrO_3$ compound obtained in our laboratory in the form of crystals or ceramics is systematically studied, and the properties of its antiferroelectric structure are constantly surprising.

Indeed, a year ago (2021), it turned out that its antiferroelectric properties are not the only ones and that ferrielectric (not ferroelectric) properties, extremely rare among hundreds of ABO_3 perovskites, may be present in this connection. This was shown by computer simulations, which concluded that polar ferrielectric properties should occur below room temperature (300K) while undermining the treatment of the ground state of $PbZrO_3$ as the antiferroelectric state.

Our preliminary studies of the dielectric properties and domain structure of $PbZrO_3$ crystals in the temperature range from room temperature to liquid nitrogen, used incidentally so far, showed anomalies characteristic of the phase transition in the range 260K-270K range. What came as a surprise, however, was the occurrence of an extremely weak pyroelectric phenomenon in this transition during the heating of the crystal, corresponding to the existence of polarisation of the order of several nC/cm^2 (figure to the right). This phenomenon was repeated many times, and moreover, the phase transition corresponding to it was close to the temperature of 255 K, obtained in the aforementioned computer simulations as the lowest limit of stability of ferroelectric ordering. In contrast to these simulations estimating the polarisation value at 11 $\mu C/cm^2$, the polarisation calculated from the pyroelectric phenomenon is almost 1000 times smaller.





Explaining this discrepancy is one of the goals of our research project. This is because it may be due, on the one hand, to the difficulty of obtaining polarisation saturation in a constant electric field, and on the other hand, it may be related to the existence of polar translational nano-boundaries also recently (2022) observed in $PbZrO_3$ at ambient temperature (figure to the left). The presence of such boundaries would explain the low polarisation value observed in the pyroelectric experiment because the polarisation is calculated for the entire volume of the crystal between the electrodes rather than for the volume occupied by the translational nano-boundaries. The preliminary studies, however, suggest that the phase transition occurs in a uniformly distributed phase throughout the crystal.

To understand the nature of low-temperature polarity in antiferroelectric $PbZrO_3$, dielectric spectroscopy, pyroelectric, Raman and Brillouin light scattering phenomena, second harmonic generation, and nano-structural studies will be carried out. The experiments will be carried out on pure and doped in A and B substructures of $PbZrO_3$, as well as on a related antiferroelectric crystal $PbHfO_3$, also pure and doped. The crystals will be grown in Polish laboratories, and part of the experimental research will be carried out in cooperation with research centres in the UK, Germany, Korea and China (like high transmission electron microscopy). If the nature of the ferrielectric macro-order is confirmed, it would mean that the phase diagrams of ABO_3 perovskite antiferroelectrics and the resulting solid solutions, such as PZT, which is ubiquitous in practical applications, will need to be revised. It will also certainly affect how new functional materials are modelled and searched for, i.e. it will greatly expand the possibilities of materials engineering. It can be said that confirmation of the long-range ferrielectric ordering will open a new chapter in the study of ABO_3 perovskites.