Weak low-temperature polarity in a $PbZrO_3$ single crystal

K. Roleder, G. Catalan, A.M. Glazer, J. S. Baker, J.-H Ko, F.H. Naqvi, S.B. Junaid,
A. Majchrowski, Z. Trybuła, J. Zaręba, I. Lazar, D. Kajewski, J. Koperski, A. Soszyński

Supplement Material 1

Dielectric measurements

The dielectric measurements of the ceramics and single crystals were made on samples coated with silver paste electrodes. The dielectric measurements were conducted using a standard capacitance method. An Agilent 4192A impedance analyser was used to measure the capacity C and conductance G in parallel circuit mode and at an AC electric-field strength of 0.1 kV/cm. Experiments were carried out in a Linkam THMS600 stage adapted to the dielectric measurements under an AC electric field. The real ε' and imaginary ε" parts of the permittivity were calculated from the relationship $\varepsilon'=C/C_0$ and $\varepsilon''= G/2\pi fC_0$, where C and G are, respectively, the capacity and conductivity of the sample. C_0 is a vacuum condenser with sizes equal to the crystal surface, thickness and the free space permittivity ε_0.

Pyroelectric measurements

The pyroelectric current measurements of the ceramics and single crystals were made on samples coated with silver paste electrodes and recorded by a Keithley 6514 System Electrometer on heating at a constant rate of 3 K/min. The measurements were carried out in a Linkam THMS600 stage adapted to the pyroelectric measurement after poling in a DC electric field in the range 85 K to 350 K. Prior to the measurement, the sample was poled in a DC external electric field of 10 kV/cm applied at 300 K and subsequently cooled in this field to 80 K, at which point the field was switched off. After 1h at 85 K, when time changes of the depolarising current could be neglected, the heating of samples at a 3 K/min rate started, and the pyroelectric current was measured. Such measurement conditions were used for PZ ceramics and single crystals. To minimize the potential influence of water on spurious thermally-stimulated currents, before the experiments, the samples were heated to 400 K and only then cooled to low temperatures in a vacuum.

Optical studies

Observations of the domain structures of a $PbZrO_3$ (PZ) single crystal were made using the Metripol (Oxford, UK) technique described elsewhere [*]. This technique measures an orientation angle φ, the extinction angle normally observed in polarising microscopy. A feature of the Metripol is the visualisation of optical indicatrix orientations. These orientations are presented as a coloured map, in which different colours are related to different values of angle φ, denoting an inclination of the slow (longer) axis of the indicatrix to the horizontal direction of the microscope stage. The distribution of these orientations can be plotted based on such maps. Each point in such a histogram corresponds to the orientation distribution calculated for a 1^{o} interval. Measurements of the optical properties of the PZ single crystal were carried out from 85 K to 350 K. The temperature was controlled to a precision of 0.1 K, and measurements were performed at a temperature rate of 1 K/min.

[*] K. Roleder, A. Majchrowski, I. Lazar, R. W. Whatmore, A. M. Glazer, D. Kajewski, J. Koperski and A. Soszyński. Monoclinic domain populations and enhancement of piezoelectric properties in a PZT single crystal at the morphotropic phase boundary, Phys. Rev. B **105**, 144104 (2022).

Raman scattering

The Raman scattering measurements were carried out using a conventional Raman spectrometer (LabRam HR800, Horiba Co., Japan) in the frequency range of 10 cm^{-1} to 700 cm^{-1}. A low-frequency notch filter was installed on the Raman spectrometer, allowing the lowest frequency in the spectra to be 10 cm^{-1}. A diode-pumped solid-state laser with a wavelength of 532 nm was used to excite the single crystal. Before taking measurements, a silicon standard sample with a single peak at 520 cm^{-1} was utilised to calibrate the Raman spectrometer. The temperature measurements were carried out using a Linkam stage (THMS600) with temperature stability of 0.1°C in the range 83K to room temperature. For each measurement, enough time was allowed for thermal equilibrium once the desired temperature was reached. All measurements were conducted with an optical microscope BX41 (Olympus, Japan) equipped with a 50-magnification objective lens and backscattering geometry. In this geometry, scattered light is captured simultaneously along the same route as the incident light.

Second harmonic generation

Temperature-resolved second harmonic generation (SHG) study was performed in 80 K – 300 K on powdered and multidomain single-crystal, using a Coherent Astrella Ti:sapphire laser system regenerative amplifier providing femtosecond laser pulses (800 nm, 75 fs) at a 1 kHz repetition rate. The laser fluence at samples was equal to 0.46 mJ/cm^2. A powdered sample was obtained by crushing the single crystals of PZ with a spatula, followed by sieving through an Aldrich mini-sieve set into a microcrystal size fraction of 125–177 μm. Next, the size-graded sample was fixed between microscope glass slides to form a tightly packed layer, sealed, and mounted to the horizontally aligned sample holder. No refractive index matching oil was used. In the case of the single crystal, the sample was mounted on a glass slide. Crystal plane (001) was parallel to the glass slide surface. The employed measurement setup operated in the reflection mode. Specifically, the laser beam delivered from the regenerative amplifier was directed onto the sample at 45^o to its surface. An Ocean Optics Flame T fibre-coupled CCD spectrograph with a 200 μm entrance slit recorded the spectra. Scattered pumping radiation was suppressed using a Thorlabs 750 nm short-pass dielectric filter (FESH0750). Temperature control of the sample was performed using a Linkam LTS420 heating/freezing stage, with a temperature stability of 0.1 K.