Probing the Giant Piezoelectric response of $PbZn_{1/3}Nb_{2/3}O_3$ at the Atomic Scale

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Piezoelectric materials, which convert mechanical to electrical energy (and vice versa), are intensively used for technological applications (sensors and actuators in medical imaging, telecommunication and ultrasonic devices). Among them, ultrahigh performance can be obtained in the lead mixed perovskite single crystal materials of general formula *AB'B''*O_3, i.e. the $PbZn_{1/3}Nb_{2/3}O_3$ (PZN) and $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) systems. However, the mechanism underlying the ultrahigh performance of these materials at the atomic scale is not clear at all and particularly the role of the *B'* and *B''* atoms, which are known to be at the origin of the polar shifts leading to the piezoelectric response. Moreover, the electric field

dependence of these polar shifts is the key issue to give the appropriate atomic scale picture of this functional material under “in-situ” conditions as in technological applications. Here we report an “in situ” Extended X-ray Absorption Fine Structure (EXAFS) study as a function of the electric field on PZN single crystal. We show that the strongly polarized Nb-O bonds are aligned along <011>, while a small reversible polar shift occurs for Zn in the direction of the electric field, i.e. positive or negative. As the Zn-O polar shift produced in the direction of the electric field is reversible, it is proposed to be at the origin of the switching of the ferroelectric polarisation when the electric field is reversed. Additionally, this small polar shift can be obtained with a modest electric field which creates a favourable energetic situation for the associated alignment of the strongly polarized Nb-O bonds and therefore accounts for the large piezoelectric effect in PZN. These results will be useful for the design and optimization of higher performance materials.

An “in situ” EXAFS study as a function of the applied electric field was undertaken on giant piezoelectric PZN single crystals at both the Nb and Zn *K* edges to understand the atomic scale behavior of the *B*-site atoms under the conditions of use in technological applications. We find that the small Nb atoms are at the origin of highly polarized orthorhombic Nb-O bonds which are aligned in the poled state. Alignment of the dipoles will be induced by a small polar shift of the Zn atoms under electric field, which is at the origin of the small E_C of PZN and thus explains the giant piezoelectric response. As this small polar shift is found to be reversible as a function of the electric field, it is therefore at the origin of the polarisation flipping when the direction of the electric field is reversed.

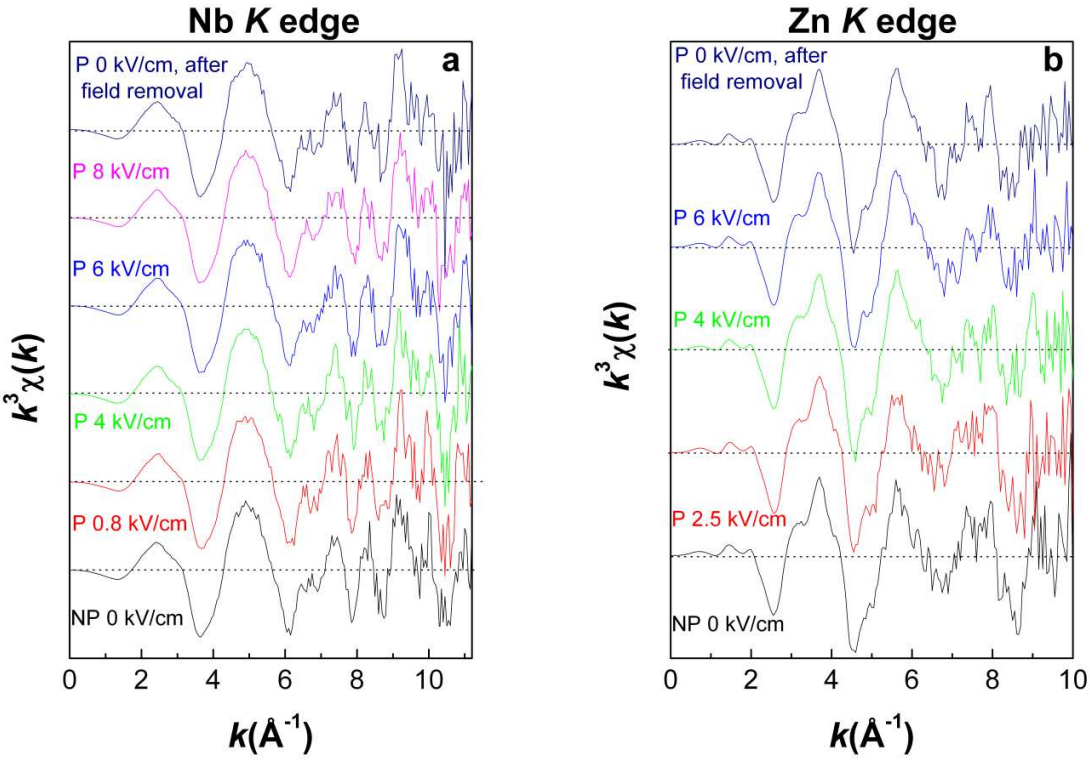

Figure 1 | EXAFS spectra of $PbZn_{1/3}Nb_{2/3}O_3$ perovskite as a function of the electric field. a, Nb *K* edge spectra **b**, Zn *K* edge spectra. NP and P accounts for Non Poled and Poled State

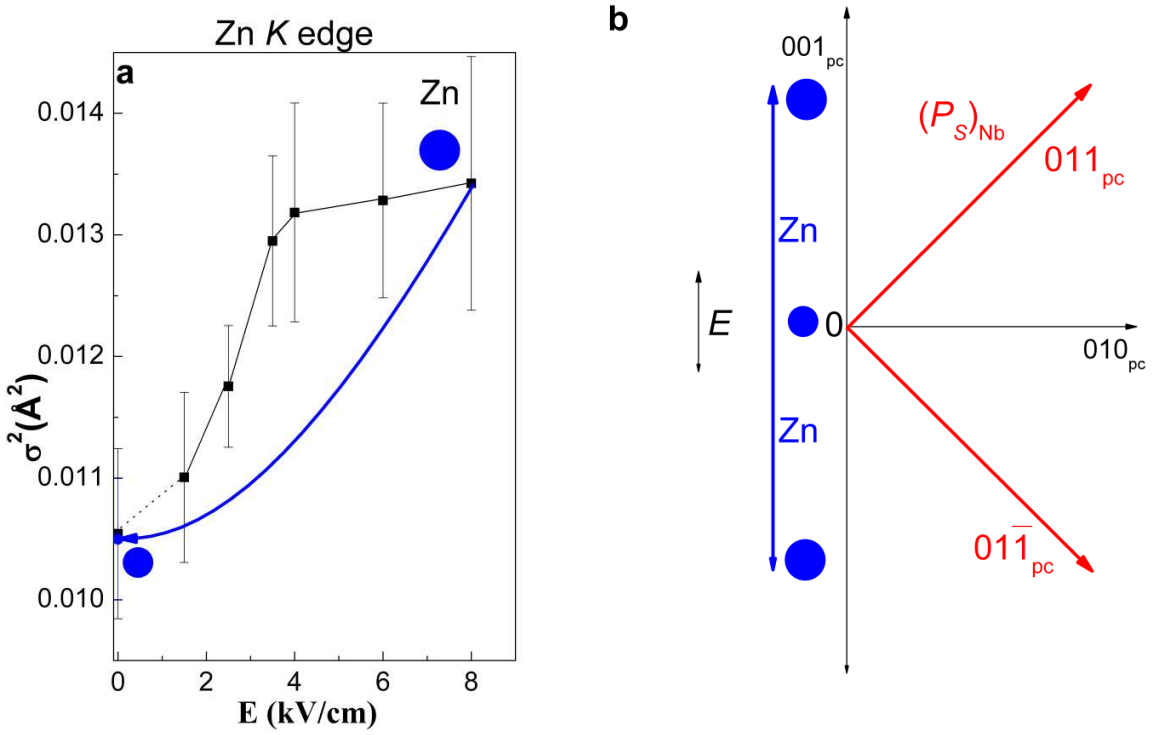

Figure 2 | **a,** electric field dependence of the experimental σ^2(Zn-O) for the Zn-O atom pairs at 300 K. Filled squares correspond to points obtained on increasing field, while the filled circle corresponds the point obtained after field removed. As indicated by the dotted line, different samples were used for the unpoled and the poled states. The black line and red arrow are only guides to the eye. Filled blue circle correspond to the σ^2(Zn-O) view, **b,** simplified scheme of the *B*-site behaviour under electric field in the PZN poled sample.