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# Impurity-induced resistivity of ferroelastic domain walls in doped lead phosphate

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## Abstract

The topology and the trace of ferroelastic domains, namely W walls, of Ca-doped lead orthophosphate  $(\text{Pb}_{1-x}, \text{Ca}_x)_3(\text{PO}_4)_2$  with a Ca content of 2.7% mol were studied on the monoclinic cleavage plane (100) using contact mode atomic force microscopy. Furthermore, conducting atomic force microscopy was applied using a bias voltage across the cantilever and the sample inducing a tunnelling current. As a reference a pure lead phosphate crystal was used. Only the Ca-doped lead phosphate crystals showed a considerable difference in conductivity between walls and the bulk. The conductivity in the bulk was found to be approximately 7% higher than in the domain walls. The experimental results show that ferroelastic domain walls of atomistic width can work as barriers to dielectric transport.

## 1. Introduction

Ferroelastic crystals display characteristic domain patterns on a mesoscopic length scale because of the symmetry reduction from a paraelastic supergroup to a ferroelastic subgroup. The interfaces between geometrically different orientation states, i.e. the domain walls, are visible under the optical microscope as sharp lines although the spatial expansion of such walls is of the order of some nanometres. Pure lead phosphate  $\text{Pb}_3(\text{PO}_4)_2$  is one of the best-studied model systems with precisely determined strain tensor components and ferroelastic domain structure [1–3]. The physical properties of lead phosphate crystals can be strongly renormalized by impurities; e.g., usually the critical temperature will change and defect tails

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in the thermal evolution of the order parameter occur [4]. The origin and arrangement of domain structures in ferroelastics is well known since Aizu's (1969) work on ferroelastic behaviour [5]. Detailed studies of wall profiles, wall patterns and wall–wall interactions in ferroelastic materials have been carried out within the last few decades [1–3, 6, 7]. Only recently, however, have investigations of transport properties of domain walls become a new study area practically and theoretically [8–10].

Recent experimental studies revealed new transport properties along domain walls. Aird and Salje [8, 9] used sodium vapour for the doping of domain walls in  $\text{WO}_3$  and found the first experimental evidence of different ion conductivity in the wall compared with the bulk. The authors observed that doping with sodium of domain walls in tungsten oxide leads to two-dimensional superconductivity.

Theoretical studies and numerical models based on the concept of the reorientation of the order parameter inside the domain wall show that the transport properties of domain walls strongly depend on the local elastic interactions and the crystal structure in the wall. Hence, Lee *et al* [10] developed a simple model, which undergoes a tetragonal-to-orthorhombic transformation by shearing. The resulting transport properties of domain walls and bulk show that it is possible to create a chemical microstructure using domain walls as a doping path into the crystal. Alternatively, domain walls can be used as a barrier to diffusion.

The ferroelastic domains in lead phosphate are monoclinic deformation states of the rhombohedral high-symmetry phase corresponding to the sequence from paraphase to ferrophase. In soft ferroelastic materials, such as lead phosphate, different domains can be reoriented by the application of external shear stress. The orientation of the walls is correlated with pseudo-symmetry elements in the ferrophase.  $W$  walls, the only type of wall considered in this paper, represent pseudo-mirror planes (namely  $(11\bar{3})$  and  $(1\bar{1}1)$  in the monoclinic phase orientated perpendicular to the cleavage plane  $(100)$ ). The interfaces are described as plane walls with an orientation predictable from the lattice parameters of the system and the ferroelastic strain.

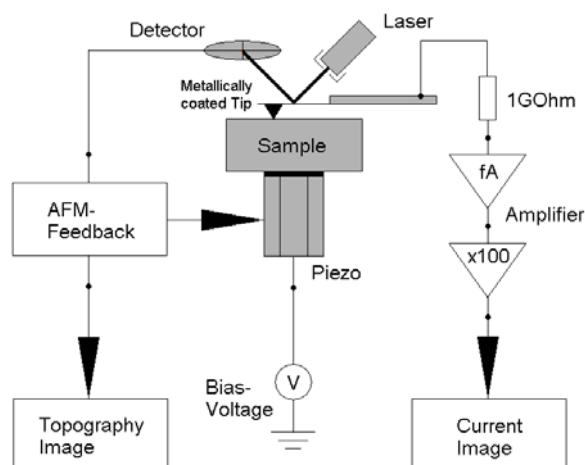
The walls separate different orientation states of the monoclinic lattice and each domain can be described by atomic displacements. Therefore, inside the wall the magnitude of the displacements might go to zero. The order parameter will therefore gradually change inside the domain walls according to the function  $Q = \tanh(x/W)$ , where  $Q$  is the order parameter,  $x$  the spatial variable and  $W$  the wall width. In geometrical terms, the lattices on either side of the wall correspond to each other via a simple rotation (referred to a coordinate system linked to the wall) [11].

Wruck *et al* (1994) investigated the thickness of  $W$  walls in pure lead phosphate at room temperature by using x-ray diffraction methods [1]. The experimental value that they found was around ten unit cells. Corresponding data were observed by Bismayer *et al* [3, 13] for lead phosphate–arsenate crystals. In this study we are interested in the conduction properties of ferroelastic domain walls of doped lead phosphate.

We focus our examination on Ca-doped lead phosphate  $(\text{Pb}_{3-x}, \text{Ca}_x)(\text{PO}_4)_2$  with  $x_{\text{Ca}} = 0.027$ . The crystals were grown by the Czochalski method. Pure lead phosphate  $\text{Pb}_3(\text{PO}_4)_2$  was used as the reference material. The aim of this study is to determine the correlation of the topography and electric conductivity of the  $W$  domain walls compared with the bulk using a modified scanning force microscope.

## 2. Experimental details

A crystal of Ca-doped lead phosphate  $(\text{Pb}_{1-x}, \text{Ca}_x)_3(\text{PO}_4)_2$  and, for comparison, a crystal of pure lead phosphate,  $\text{Pb}_3(\text{PO}_4)_2$ , with a freshly cleaved surface parallel to the monoclinic plane



**Figure 1.** The set-up of the CAFM system. The system allows one to visualize the topography and current image simultaneously. The optimal bias voltage was 30 V.

(100) were mounted on sample holders using liquid silver for fixing and to give a conductive contact at the back of the crystals.

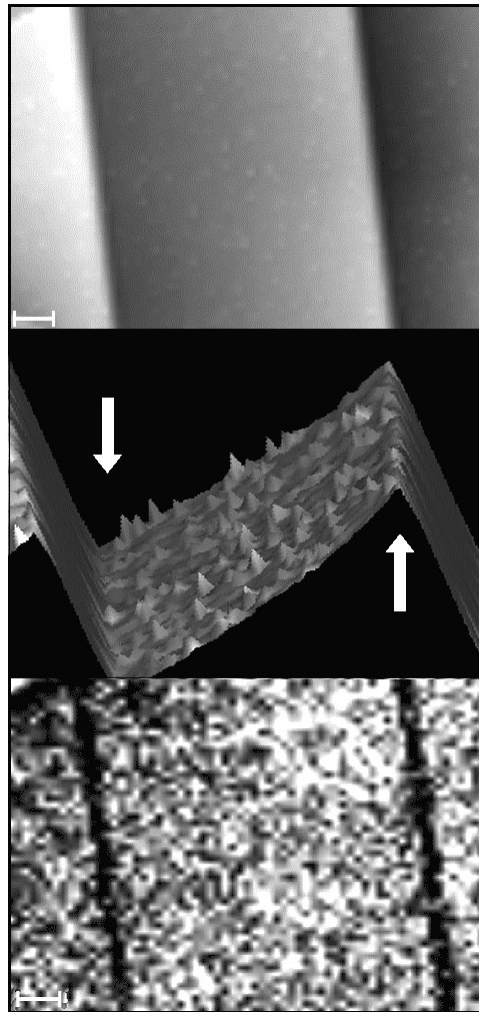
The topography and electric conductivity were determined using a modified scanning force microscope. The basis of this system consists of Multimode/Nanoscope-3a from Digital Instruments equipped with a highly sensitive current amplifier (LCA-1K-5G from FEMTO). The amplification factor of  $5 \times 10^9 \text{ V A}^{-1}$  is enhanced by an additional stage allowing amplifying by  $5 \times 10^{11} \text{ V A}^{-1}$ . This equipment enables us to measure currents between 20 fA and 20 pA. In figure 1 the principal function of the conducting AFM (CAFM) system is displayed. Similar instruments were previously used for the electric characterization of thin oxide layers [12].

All measurements were carried out under ambient conditions and at room temperature. A bias voltage was applied to the back of the sample with values between 10 mV and 50 V. Simultaneously, the sample surface was scanned in contact mode using a conducting cantilever. This procedure allows two-dimensional visualization of the topography and determination of the local conductivity at the same location with a spatial resolution of about 200 nm. In order to guarantee stable conductivity of the cantilever, highly doped silicon tips with a subsequent metallic coating (type MESP from Nanosensors) were used.

Low loading forces of 100 nN and a slow scan velocity of  $<10 \text{ nm s}^{-1}$  were chosen to decrease the abrasion of the sensor. We found an optimal bias voltage of 30 V to give a good contrast in the current image. Higher values of the applied electric field lead to an overload at the crystal surface followed by destruction. The procedure described allowed conductivity studies of the domain walls and of the bulk material.

The stoichiometry of the sample was measured using a CAMECA SX 100 microprobe. Averaging over ten measurements yields a chemical composition of  $(\text{Pb}_{3-x}, \text{Ca}_x)(\text{PO}_4)_2$  with  $x_{\text{Ca}} = 0.027 \pm 0.0004$ . The Ca reference was chemically pure andradite. The spatial resolution of the microprobe analysis was not sufficient to allow determination of the doping level of the W walls.

The lattice parameters of  $(\text{Pb}_{3-x}, \text{Ca}_x)(\text{PO}_4)_2$ ,  $x_{\text{Ca}} = 0.027$ , were determined from 19 Bragg peaks using an X-Pert 500 powder diffractometer (Siemens) with  $\text{Cu K}\alpha_1$  radiation.

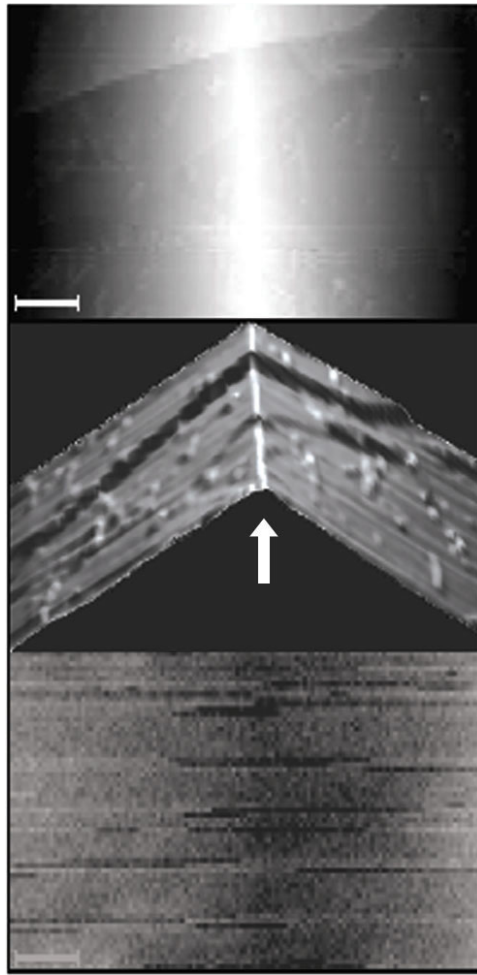


**Figure 2.** All images show the same sector. The scale bar is  $1\ \mu\text{m}$ . Top: the topological arrangement of the W domain walls in Ca-doped lead phosphate. The lines indicate the walls orientated perpendicular to the surface which is the (100) cleavage plane. Middle: a 3D surface plot forming a zigzag profile (see also [2]) with walls marked by arrows. Bottom: the conductivity of the W walls and the bulk material. Dark lines indicate the lower conductivity of the walls. The difference in brightness is due to current difference of  $40\ \text{fA}$  (the noise level is  $\pm 10\ \text{fA}$ ).

### 3. Results and discussion

The topological arrangement of the W walls is shown in figure 2 (top). The angle between the wall and the crystal surface (001) was calculated from the lattice parameters of  $(\text{Pb}_{3-x}, \text{Ca}_x)(\text{PO}_4)_2$ , which were determined as  $a = 13.800(9)\ \text{\AA}$ ,  $b = 5.688(6)\ \text{\AA}$ ,  $c = 9.423(8)\ \text{\AA}$ ,  $\beta = 102.41(7)^\circ$ .

The resulting angle between (100) and the pseudo-mirror plane  $(11\bar{3})$  is  $89.36^\circ$ . This leads to a zigzag shape for the trace of the W walls on (001) with an angle of  $178.72^\circ$ . Patterns for such multidomain systems were recorded previously by Bosbach *et al* [2], for pure lead phosphate, and by Bismayer *et al* [13], for doped compounds of the same type.



**Figure 3.** All images show the same sector. The scale bar is  $1\ \mu\text{m}$ . Top: the topological arrangement of W domain walls in pure lead phosphate. Middle: a 3D surface plot. The wall is marked by an arrow. Bottom: the conductivity of the W walls and the bulk material. In the case of pure lead phosphate no lines occur indicating positions of domain walls in the conductive modes. No remarkable difference between the conductivities of the wall and bulk could be detected.

The conductivities of the domain bulk and domain walls of a crystal section are displayed in figure 2 (bottom). The conductivity in the bulk was found to be approximately 7% higher than that in the domain walls. The current via the silicon tip to the crystal surface was 600 fA. The variation of the brightness between the wall and bulk areas in figure 2 (bottom) is caused by a difference in current of 40 fA. A maximum bias voltage of 30 V was used without destroying the crystal. The corresponding maximum charge density at the needle tip was  $32\ \text{As m}^{-2}$ . In the reference material (pure lead phosphate) no significant difference between the bulk and wall resistivities could be detected (figure 3, bottom). We therefore conclude that Ca doping may influence the conductivity of the W walls. In fact, the signal recorded on the walls includes contributions from the neighbourhood of the walls. Hence, contributions from the neighbouring bulk conductivity cannot be excluded because the lateral resolution of the cantilever tip is less than the wall width [1]. Impurities of calcium ions may, however, be

pinned in the wall or in its close vicinity. The comparison between the bulk and wall (plus bulk) conductivities clearly yields a lower conductivity measured along the walls. It is not clear what transport species we were measuring. We could be measuring the transport of calcium ions, with  $\text{Pb}^{2+}$  ions being oxidized to  $\text{Pb}^{4+}$  when a  $\text{Ca}^{2+}$  ion leaves the crystal. We could also be measuring electron or hole conductivity if the crystal is non-stoichiometric (with the stoichiometry varying across the domains). Further studies will be undertaken in order to clarify what transport it is.

Our experimental results give the first evidence that the conductivity of domain walls in Ca-doped lead phosphate is reduced compared with that in the bulk and that ferroelastic domain walls can act as barriers to dielectric transport. Our results are in excellent agreement with theoretical studies [8], which predict that it is possible to use domain walls for the creation of chemical microstructures. The fact that walls and bulk material show different types of dielectric transport and different diffusion rates could also be very useful for future technological applications on atomistic length scales, considering the widths of such walls.

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