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Direct observation of ferroelectric domain formation by environmental scanning electron microscopy

A. Reichmann [a,*], A. Zankel [a], H. Reingruber [a], P. Pölt [a], K. Reichmann [b]

[a] *Institute for Electron Microscopy, Graz University of Technology, Steyrergasse 17, 8010 Graz, Austria*
[b] *Christian Doppler Laboratory for Advanced Ferroic Oxides, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria*

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Abstract

The evolution of the ferroelectric domain pattern in donor-doped barium calcium titanate during heating and cooling across the Curie transition temperature was imaged by orientation contrast imaging using an environmental scanning electron microscope (ESEM) equipped with a heating stage. The vanishing of the ferroelectric domains above the transition temperature as well as their recurrence during cooling was observed. The domain pattern of the sample largely remained the same, confirming that domain orientation is determined by elastic energy conditions (clamping), which scarcely change within the investigated temperature range. In a few cases a change in the domain pattern of single grains was observed during heating and cooling.

Keywords: Electron microscopy; Ferroelectric properties; Thermal properties; $BaTiO_3$; Domain structure

1. Introduction

A domain structure within single crystals, polycrystalline ceramics or thin films is a commonly observed feature of ferroic materials (ferroelectrics, ferromagnetics and ferroelastics) below a typical transition temperature usually referred to as Curie point. On cooling below the Curie transition temperature T_C, the crystal structure changes from a centrosymmetric to a non-centrosymmetric structure. For example, at ~120 °C $BaTiO_3$ transforms from a cubic paraelectric structure with the titanium ion octahedrally coordinated by oxygen to a tetragonal ferroelectric structure with the titanium ion off-centred relative to the oxygen anions causing a spontaneous polarization of the material. During this cubic-to-tetragonal transformation the titanium ion has the opportunity to shift in six equivalent directions. The displacement of the titanium species in one unit cell affects the displacement of the titanium species in neighbouring cells, so ferroelectricity is considered to be a cooperative ordering effect. This results in the formation of regions of homogeneous polarization in the material, referred to as domains.[1] The formation of domains is a result of the minimization of electric stray field energy and/or elastic energy. In the case of ferroelectric domains this process depends on the building and mobility of domain walls, elastic stress fields, polarization charges, free charge carriers, point defects (vacancies, substituents) as well as dislocations.[2]

In ferroelectric single crystals the electrical stray field energy caused by the non-compensated polarization charges is reduced by the formation of domains following head-to-tail conditions (yielding 180° domain walls), whereas in polycrystalline ceramics the domain structure of each grain is considered a result of the elastic clamping conditions given by the surrounding grains (ultimately an outcome of the thermal processes that a ceramic body has to undergo).[3] Since the elastic energy can be reduced only by non-180° domain walls, a domain pattern consisting of mainly 90° domain walls for tetragonal symmetry should be formed. In coarse grained ceramics this yields a banded domain structure, which turns into a lamellar structure when the grain size decreases.[4]

These domains can be easily imaged by a scanning electron microscope (SEM) choosing appropriate operating conditions and specimen preparation (e.g. etching). For example, Zhu et al.[5] have successfully observed a stable contrast image of antiparallel domains in poled $LiTaO_3$ crystals using ESEM. The evolution

* Corresponding author. Tel.: +43 316 873 8347, fax: +43 316 811 596.
E-mail address: angelika.reichmann@felmi-zfe.at (A. Reichmann).

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of a domain structure during the phase transition has not been investigated by SEM because of the need for controlled heating and cooling across T_C. Other experimental setups for the imaging of domain evolution were combined with light microscopy,[6] which is limited in resolution, or scanning probe techniques.[7,8]

For this study we used an environmental scanning electron microscope (ESEM) equipped with a specially designed heating stage.[9] Different contrast mechanisms can be used for imaging ferroelectric domains.[10] In our study the domains were visualized by orientation contrast (OC) due to electron channelling. The regular arrangement of atoms in crystalline solids can influence the backscattering of electrons as compared to the near-random three-dimensional distribution of an amorphous solid. Paths of very low atomic density ("channels", generally low index directions) are found, which permit at least a fraction of the beam electrons to penetrate more deeply into the crystal before beginning to scatter. This reduces the probability that they will return to the surface as backscattered electrons. For other crystal orientations, a denser atom packing can be found, and the beam electrons begin to scatter immediately at the surface, increasing the backscattering coefficient. The modulation of the backscattering coefficient between the maximum and the minimum channelling cases differs by only about 5%. Nevertheless, this electron channelling contrast can be used to derive microstructural information. This contrast is carried by the high-energy fraction of the backscattered electrons, and so a solid state detector with the specimen set normal to the electron beam was used to maximize the signal.[11]

The model material for this study was an yttrium-doped $(Ba,Ca)TiO_3$ polycrystalline ceramic with a T_C at 120 °C because imaging is facilitated by the relatively large grains of around 5 μm with a well developed domain structure. This material is semiconducting and applied in large volume as positive temperature coefficient resistors (PTCRs). At high temperatures this material acts as an insulator due to the high resistivity of the grain boundaries. Space charges build up near the oxidized grain boundaries during sintering of the ceramic in oxidizing atmospheres. These double Schottky barriers are potential barriers for the conducting electrons. Below the Curie transition temperature the grains have ferroelectric domains, which are highly polarized. These polarization fields can completely compensate the action of the Schottky barriers and as a consequence the material becomes electrically conductive.[12] The aim of this study was to observe in situ the vanishing of the domain structure above T_C and the re-emergence of domains when cooling below T_C and to clarify whether mechanical stresses cause a kind of mechanically predetermined polarization orientation and hence force a fixed domain pattern, or if spontaneous polarization is random in orientation leading to a varying domain pattern after each temperature cycle.

2. Experimental

Commercially available samples of PTCR ceramics consisting of $(Ba,Ca)TiO_3$ doped with yttrium (0.5 mol%) and manganese (0.1 mol%) were used for this investigation. The Curie transition temperature for this composition is at 120 °C.

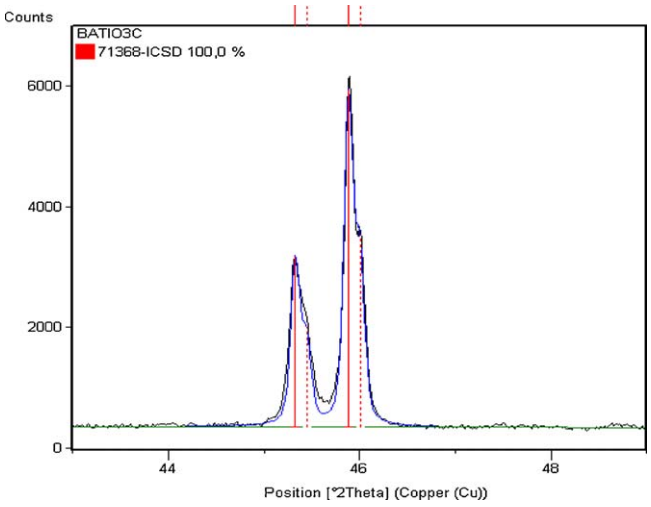

Fig. 1. X-ray diffraction pattern (measured and calculated after Rietveld refinement) of the 002/200 doublet of the sample after polishing. Vertical lines indicate the position and the intensity of the reference pattern.

Discs of 13 mm in diameter and 3 mm in height were ground on silica carbide paper, finished with 4000 grit and then polished using a 0.25 μm diamond paste. The samples were mechanically fine polished using 0.04 μm SiO_2 emulsion on a vibration-polishing machine for a duration of 12 h to obtain the smooth surface required for good-quality OC (orientation contrast) images. To check whether the surface treatment influences domain orientation or induces stresses on the sample surface an X-ray diffraction spectrum was measured from the 002/200 doublet (Fig. 1). Measurement was carried out on a PANalytical PW 3710 diffractometer equipped with Anton Paar TTK camera with adjustable sample holder (correction of sample height). A sharp doublet with correct intensity ratio (compared to a pattern by Tiwari et al.[13] obtained from $Ba_{0.88}Ca_{0.12}TiO_3$) is detected, which indicates that no preferred orientation or amorphisation was generated during grinding and polishing. This simple preparation procedure yields the same image quality as ion milling, which was applied by Grüner et al.[10] for imaging domains in ferroelectric ceramics.

The heating experiments were carried out in an environmental scanning electron microscope (ESEM) equipped with a field emission gun (FEG) from FEI (Eindhoven, NL) using the low vacuum mode with water vapour as the imaging gas and a pressure of around 0.3 Torr. Although better images can generally be obtained by working in high vacuum mode, the low vacuum mode prevents electric charging of the sample during the transition from semiconducting to non-conducting behaviour. Free ions generated by collisions between moving electrons and the neutral water molecules neutralize the beam deposited surface charge in insulators.[14]

The sample was clamped to a modified heating/cooling platform (temperature range from −120 °C to 200 °C) developed by Gatan, Inc. (Pleasanton, CA, USA)[9] and heated from 80 °C to 190 °C (temperature measured at the heating platform) in 10 °C steps. The temperature of the sample itself was directly measured on its surface by a NiCr/Ni thermocouple attached to it. Good thermal contact between sample and thermocouple was

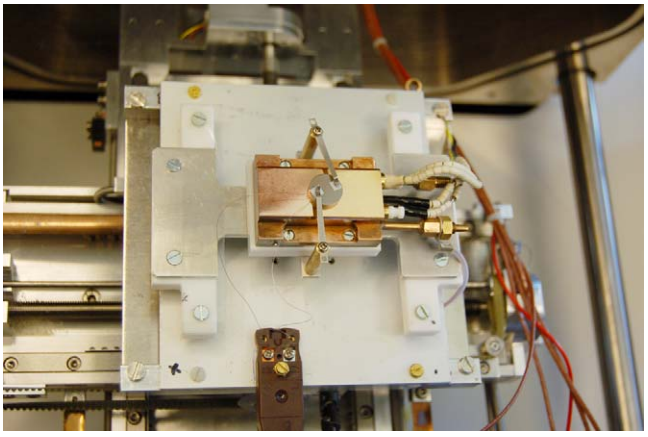

Fig. 2. Sample stage with the sample clamped to the heating block.

provided by a leaf spring clamp (Fig. 2). To avoid thermal contact between the spring and the thermocouple a teflon pad was mounted in between. The OC images were recorded using a solid state backscattered electron detector directly mounted on the pole piece of the microscope. A relatively large working distance of 11 mm was chosen to protect the detector from damage caused by heat radiation.

3. Results and discussion

The polishing methods developed for electron backscattering diffraction (EBSD) analyses and FEG-SEMs equipped with a solid state backscattered electron detector make it possible to image grains with domain structure in high quality. For this purpose the surface of the ceramic sample must be free of any structures that give a topographic contrast. A high probe current is applied for imaging. Because of this high probe current it was necessary to blank the electron beam during heating in periods where no image was recorded. Otherwise the scanned surface will be contaminated by carbon originating from organic impurities within the microscope itself. This contamination acts like an evaporated carbon layer and degrades image quality.[15]

Fig. 3a shows the microstructure immediately before the start of the heating experiment. The crystallites have an average grain size of approximately 5 μm in diameter and exhibit mainly wedge-shaped lamellar domains. These domains are a common microstructural feature in most ferroelectric materials

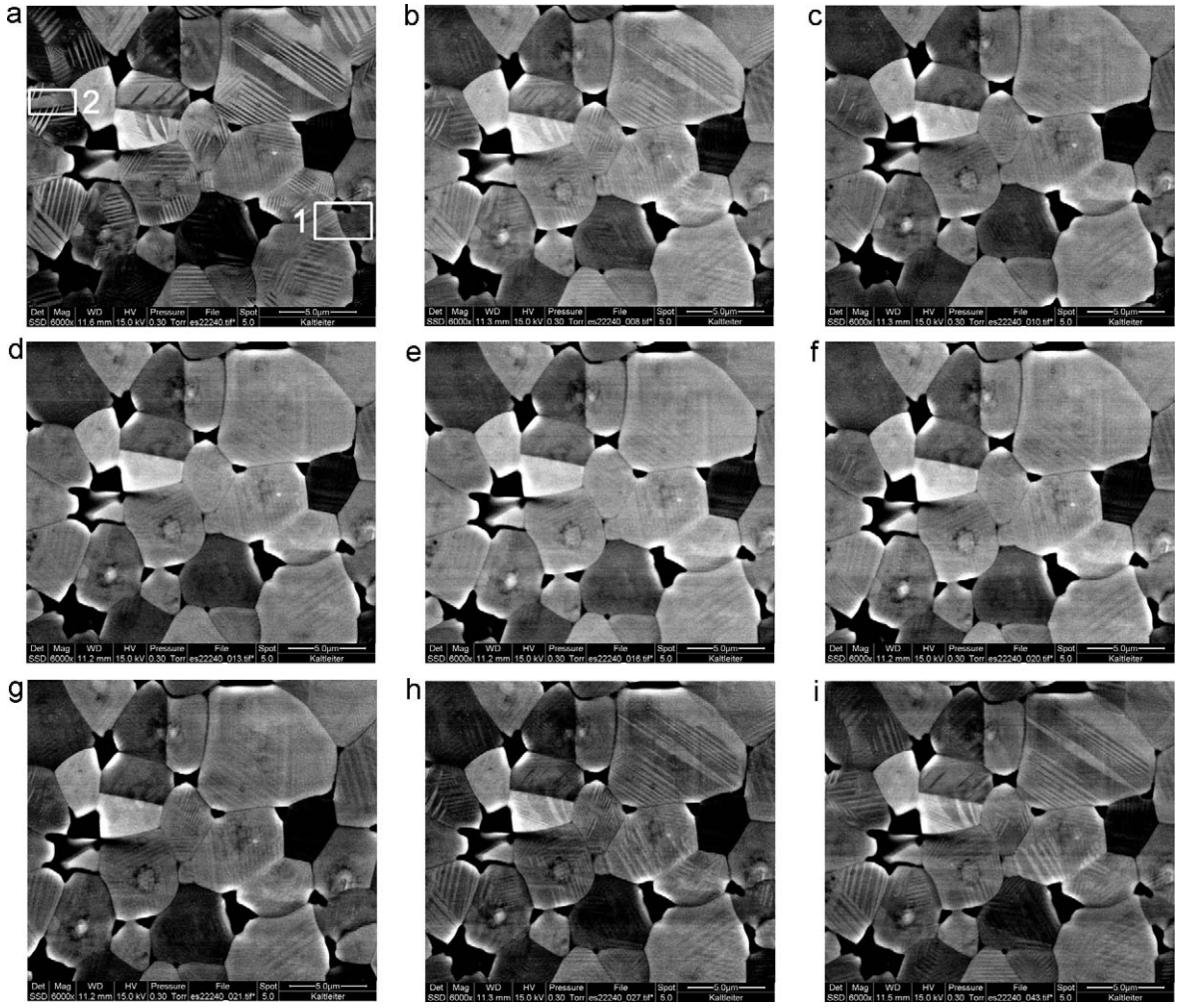

Fig. 3. Orientation contrast images of the polished ceramic sample at different temperatures. (a) 40 °C, (b) 102 °C, (c) 115 °C, (d) 124 °C, (e) 134 °C, (f) 118 °C, (g) 113 °C, (h) 98 °C, (i) 40 °C.

and are known to occur when the 90° walls terminate within the grain.[4,6] Area 1 in Fig. 3a reveals domains which cross grain boundaries while maintaining their orientation. This is a characteristic feature of coarse grained barium titanate.[4]

The variation of the domain structure with temperature is shown by the image series in Fig. 3a–i. Area 2 in Fig. 3a–c shows that the domains become blurred and seem to disappear gradually as the temperature rises. In some cases the domain structure changes during the heating process, indicating a release of elastic clamping energy during heating. In this special grain (Area 2) the domains are interrupted by a zone with no visible domain structure. This zone disappears with increasing temperature. At a temperature of about 124 °C (Fig. 3d) nearly all domains visible at room temperature have vanished. It is noteworthy that a weak lamellar contrast was observed even above the Curie temperature (134 °C, Fig. 3e). The first domains emerge when the temperature decreases, at about 118 °C (Fig. 3f). In most of the grains the domains appear in the same arrangement (shape and place) as before the heating process. Only small changes around the domain boundaries can be observed. An example can be found in Area 2 (Fig. 3h–i), where the structure of one grain has altered spontaneously during cooling. From these findings we can conclude that the formation of the domain pattern in this ferroelectric ceramic under the given conditions is not a random process, but determined by the minimization of the mechanical stress, which does not change substantially within the investigated temperature range. In a few grains a change in elastic energy conditions (clamping) also leads to a change in the domain pattern.

4. Summary

The evolution of domain patterns in Y-doped (Ba,Ca)TiO_3 during heating and cooling across the Curie transition temperature T_C was observed in situ in an ESEM equipped with a heating stage. The temperature of the sample was measured by a thermocouple clamped to the sample surface. Sample preparation involved polishing with silica emulsion to provide a perfectly smooth surface for orientation contrast imaging. Starting from room temperature, domains become blurred and disappear gradually when approaching T_C. Cooling from above T_C causes a recurrence of the domains in a very similar pattern as observed before heating, thus confirming that the mechanical stresses (elastic energy conditions) predetermine the domain structure and that random orientation of the polar axes during spontaneous polarization can be excluded. Only a few grains showed a change in domain pattern during heating and cooling, indicating a local change in elastic energy conditions.

Future development of this method will focus on increasing the temperature range and improving the thermal contact between sample and heating block.

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