

Imaging Domain Dynamics by Combined XRD and DMA

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BIOGRAPHY

Dr Simon Redfern is reader in mineral physics at the University of Cambridge where he obtained his PhD in 1989. His research interests focus on the behaviour of minerals and oxide materials as a function of temperature and pressure, particularly related to structural phase transitions, which he studies using a number of techniques including X-ray and neutron scattering.



ABSTRACT

The dynamic response of transformation-induced microstructures to external mechanical or electrical forces is of fundamental importance in solid-state physics, materials science and geology. The interaction of mobile ferroelectric domain walls with lattice defects is a key factor in determining the lifetime of ferroelectric memory devices. Displacement of domain walls in martensitic alloys leads to the shape memory effect. Recently, transformation twinning in perovskites has been proposed as a possible source of anelasticity in the Earth – a phenomenon responsible for the attenuation of seismic waves. So there is great interest in the dynamic response of ferroelastic domain walls to an alternating stimulus mimicking the typical characteristics of a seismic wave. We describe a new method for imaging transformation twin dynamics using combined stroboscopic X-ray diffraction, dynamical mechanical analysis, and video microscopy.

KEYWORDS

X-ray diffraction, dynamical mechanical analysis, video microscopy, microstructures, domains, ferroelectric materials.

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INTRODUCTION

Understanding the fundamental atomic-scale processes responsible for the bulk physical properties of solids has long been the aim of structural physics. Historically, there has been a strong emphasis on the understanding of the properties of crystalline materials from a structural crystallographic perspective. The majority of this work has, of course, focused on the information that can be gained from Bragg scattering of X-rays. The development of large linear and area detectors over the last decade has, however, opened up the way for rapid analysis of both diffuse and Bragg scattering over large volumes of reciprocal space.

Over this period methods have been developed for systematically exploiting position-sensitive detectors with thousands of detection channels working in parallel, and area detectors that, by parallelisation, are able to collect data at rates six orders of magnitude greater than those of traditional instruments. This means that microstructural and mesoscopic structural features such as transformation twins may now be investigated directly by laboratory X-ray scattering techniques.

Transformation twins form spontaneously on cooling through a symmetry-breaking phase transition, and may typically be imaged using polarised light microscopy (Fig 1). Each twin domain represents a degenerate orientational variant of the lattice of the low-symmetry (usually low-temperature) phase. The strain fields associated with these microstructures can also be studied quantitatively in reciprocal space as a function of temperature, in particular at temperatures near phase transitions. For example, X-ray diffraction from twin boundaries in $\text{YBa}_2\text{Cu}_3\text{O}_7$, occurring at 25-nm intervals have been readily detected, showing that the domain wall thickness is of the order of 0.55 nm [1-3]. Subsequent experiments on Al-doped YBCO showed that the rocking-curve technique (Fig 2), using Instrumentation Electronic (INEL) curved 1D position-sensitive X-ray

detectors, is capable of measuring twin walls at very sparse concentrations indeed (one wall every $10\ \mu\text{m}$ [4]).

All these data were obtained from static experiments: the applied load on the sample is usually zero, or is a fixed static stress, e.g. in the study of the effect of applied stress on the phase transition of SrTiO_3 [5]. The degeneracy of ferroelastic twin domains can be broken by application of a stress, causing growth of energetically favourable domains at the expense of energetically unfavourable domains. This is achieved by the movement of domain walls and growth or shrinkage of domains, in a similar way to the poling of ferroelectric or ferromagnetic domains on the application of electric or magnetic fields, respectively. Such elastic domains are termed ferroelastic [6]. Ferroelasticity can be defined by the response of a twinned crystal to an applied stress, and such response is also important in understanding the full energetic effects of displacive transformation, as well as understanding transformation-induced plasticity in metals.

One aspect of such twin-domain-related structural responses that is of particular interest in geophysics is its effect on the attenuation of seismic waves, usually resulting from earthquakes, caused by the anelastic (i.e. time-dependent mechanical) response of rocks and minerals to an applied stress. This results in the dissipation of elastic energy. A number of recent studies have highlighted the importance of transformation twinning as a potential source of anelasticity in ferroelastic materials subjected to alternating stress at seismic frequencies [7-9]. Displacement of domain walls results in a time-dependent macroscopic strain, potentially accompanied by massive mechanical softening and very large mechanical attenuation. Domain-wall dynamics also have great significance beyond their anelastic characteristics. For example, the interaction of mobile ferroelectric domain walls with lattice defects is a key factor in determining the life-

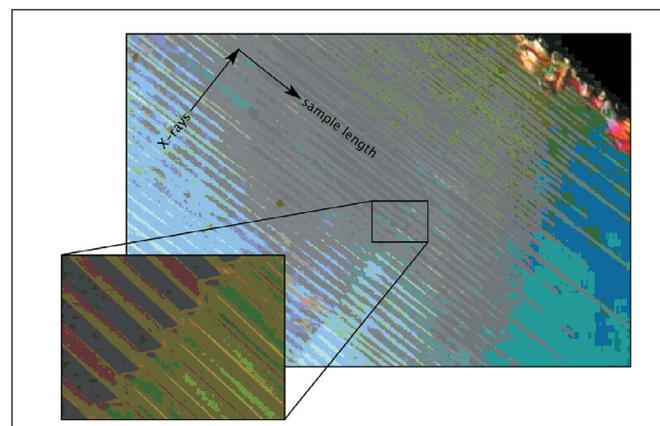


Figure 1: Polarised light micrograph the ferroelastic domain microstructure of LaAlO_3 . The inset shows a chevron arrangement of twins.

time of ferroelectric memory devices [10]. The creation and displacement of domain walls in martensitic alloys leads to the shape memory effect [11]. More pertinently, movements of domain walls are also the origin of ferroelastic hysteresis and thus define ferroelasticity.

The next step in observing strain effects, on both microstructures and the bulk, near and resulting from phase transitions was the development of a method for making diffraction observations from samples subjected to a dynamically fluctuating load. Until recently this step has not been possible, but the advent of fast multidimensional detectors and rapid switching electronics now makes it technically feasible to collect diffraction patterns from samples on time scales of tenths of milliseconds, and hence makes it possible to use stroboscopic methods to study the varying response of materials to applied stresses as a function of phase angle during the alternating cycle of a dynamically applied load.

We have implemented this step by using a combined dynamic mechanical analyser, multi-channel detector system, and fast switching data grabbing system. It allows the first ever diffraction measurements of the effects of applied stress on domain wall thickness and movement, mechanical embrittlement of engineering solids during phase transformations and time-temperature excursions, and the precise measurement of elastic modulus very close to phase transitions and subject to critical phenomena in the vicinity of T_c . All of these are simultaneous with measurement of the structure and microstructure.

SIMULTANEOUS DIFFRACTION, IMAGING, AND MECHANICAL SPECTROSCOPY

We have built a prototype instrumental method for the simultaneous measurement of elastic properties and diffraction signals from materials subjected to a dynamically modulated applied stress. The instrument is capable of simultaneous stroboscopic X-ray diffraction, video microscopy, and dynamic mechanical analysis at temperatures up to 1000 °C and as a function of frequency of applied stress in the frequency regime 10 mHz to 100 Hz. It has been used to measure the isothermal mechanical response of microstructured crystals at and near phase transitions while simultaneously measuring the ferroelastic spontaneous strain of the bulk. We are now able to observe strain effects, on both microstructures and the bulk, near and resulting from phase transitions from samples subjected to a dynamically fluctuating load.

The elements of the stroboscopic XRD-DMA diffractometer are shown in Fig 3. The DMA component is based on a standard Perkin-Elmer DMA-7e, modified to allow access of X-rays to the bottom surface of the sample. The DMA is configured in a vertical orientation at the top of the instrument, with a stress motor imparting a force to the probe, which takes the form of a three-point bending flexure rig at the heart of the diffractometer. The force imparted is computer controlled, and takes the form of an alternating stress across the fre-

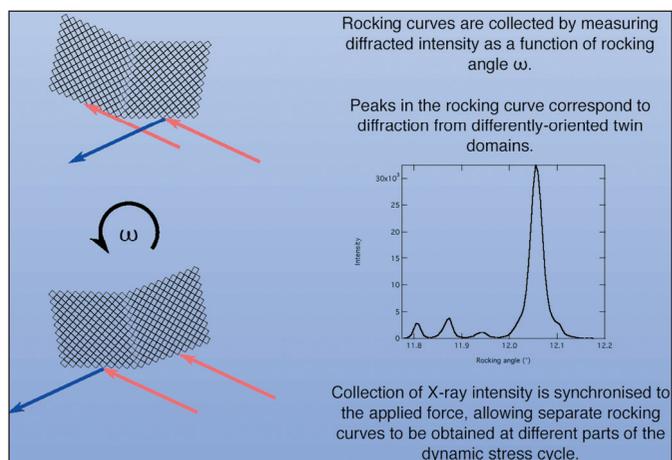


Figure 2: Rocking curves allow diffraction to be measured from each twin domain in a ferroelastic material.

quency range 0.01-50 Hz. The strain of the sample is measured by an analogue strain sensor, to a resolution of 10 nm. The sample and flexure head components are all enclosed in a thermally stable furnace with X-ray-transparent windows.

The diffractometer comprises an INEL curved position-sensitive detector (PSD), covering $120^\circ 2\theta$, and a sealed-tube X-ray source with monochromator optics and collimation system ($\text{Cu-K}\alpha_1$ radiation). A 100-mm diameter beam impinges on the lower surface of the sample, and is diffracted in reflection geometry to the detector. The X-ray source is mounted on a rigid vertically oriented optic table, centred on the sample. The source can be rotated about an axis perpendicular to the scattering plane, allowing rocking curves to be measured from the sample while it is under dynamic stress. Below the heating stage we have mounted a video camera to capture images and movies of the domain wall dynamics during in-situ measurement.

Central to this new instrument is the manner in which data from the X-ray detector and

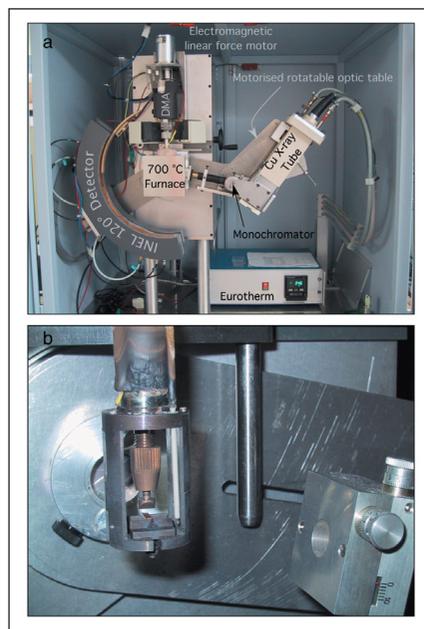


Figure 3: The combined X-ray diffraction, dynamical mechanical analysis (DMA-XRD) instrument. (a) The layout of the X-ray source, detector, furnace, and DMA components. (b) A close up of the DMA head with incident X-ray collimation.

mechanical analyser are collected in a combined manner. We employ a unique stroboscopic lock-in technique. A timing chain takes information from the dynamic mechanical analyser and passes it through a logic translator to trigger collection of the diffraction pattern at four points in the applied stress cycle. The diffraction information, extracted from the multichannel analyser of the curved PSD at four times the frequency of the sample oscillation, is then stored into one of four accumulating data files, corresponding to the diffraction pattern of the sample under each of the four conditions of applied stress at that frequency.

By altering the phase shift between the applied stress reference signal and the data collection trigger, the sample can be probed at any condition of applied stress or strain (mean stress, maximum stress, minimum stress, etc.) by diffraction. By employing a rocking experiment the diffraction (from domain walls, for example) can be observed at each state of applied stress. The sample is held within a furnace designed to control the sample temperature between ambient and 1000 °C. It allows access of the main beam and diffracted beams using an X-ray transparent window to maintain a constant controlled temperature environment at the sample. Video imaging of domain-wall dynamics is also possible for samples held at high temperature within the furnace.

DOMAIN-WALL DYNAMICS IN LaAlO_3

Lanthanum aluminate has proved to be a model system for the study of domain-wall dynamics using the XRD-DMA. The high-temperature phase of LaAlO_3 has the cubic perovskite structure, formed of a network of corner-sharing AlO_6 octahedra (Fig 4). Below about 550 °C it undergoes a phase transition, driven by rotation of the AlO_6 octahedra about one of the cubic three-fold symmetry axes. This leads to a typical domained microstructure with prevalent transformation twins developing in single crystals. Our experiments have shown that the mechanical properties of such microstructured solids show marked dispersion. In fact, data from perovskite oxides collected in the mHz to Hz frequency regime bear little relation to those measured at the frequency range of conventional ultrasonic and

light scattering techniques (i.e. MHz to GHz). This difference is caused by the stress-induced movement of transformation twins at low frequency.

High-temperature rocking curves have been collected from LaAlO_3 held under dynamic applied stress during heating from room temperature to above the critical temperature (T_c) 550 °C and back again. Diffraction measurements were made during a series of isothermal annealing steps under dynamic load. At some temperatures, rocking curves were measured at infrequent intervals over a period of days to weeks. No changes in the curves were observed as a function of time during isothermal annealing under dynamic load at a given temperature. However, major changes in the rocking curves were observed on heating or cooling (Fig 5). It seems that the microstructure is sensitive to changing temperature under dynamic load, but stable with respect to time at any fixed temperature.

This has been confirmed in a series of microscopy observations of crystals held at high temperature under dynamic load. Images of twin domain movement reveal several modes of displacement of domain walls, with changes between modes occurring upon changing stress conditions or temperature conditions. The first mode involves rapid advancement or retraction of needle domains. With increasing applied stress there comes a point when the equilibrium distance moved by the needle tips is greater than the sample width. Partial saturation occurs when there is a range of distances over which needles are free to move and/or a range of domain-wall mobilities, so that only a fraction of the available needle tips reach the sample edge during the dynamic force cycle. The force needed to enter the partial saturation regime varies with temperature, since domain walls displace more when the spontaneous strain is low (close to the phase transitions), so that saturation occurs at lower forces for temperatures close to T_c . The second mode involves the lateral translation of lamellar twin walls. Three-point-bend geometry requires that domain walls move in opposite directions at the top and bottom surfaces of the sample, resulting in rotation rather than translation of the domain wall. Adjacent walls rotate in opposite senses, so that for sufficient values of applied force they come into contact at the top and bottom surfaces, causing saturation. Our movies of domain-wall dynamics reveal each mode of deformation (Fig 6), and can be seen as animated images online at: www.esc.cam.ac.uk/astaff/redfern/domains.html

CONCLUSIONS

These experiments have demonstrated that the response of domain walls to a dynamically applied load can be resolved successfully using stroboscopic X-ray diffraction techniques, as well as simultaneous video microscopy. The microscopy is particularly revealing of changes in domain wall response for crystals held under applied load. The apparatus that we have developed is amenable to use in other, more traditional, applications of dynamic

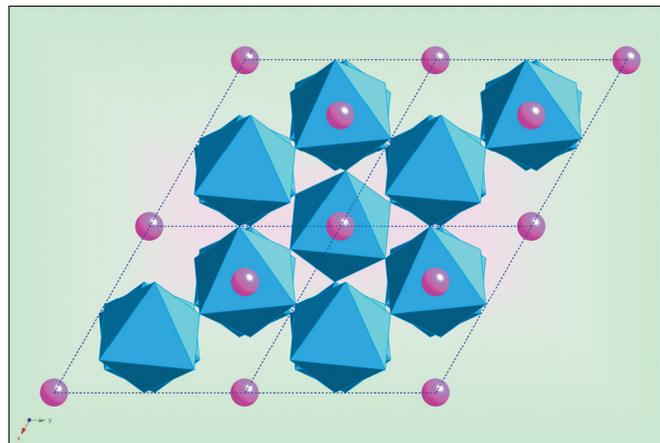


Figure 4: View of the crystal structure of rhombohedral LaAlO_3 looking down the cubic $[111]$ direction, showing AlO_6 octahedral rotations.

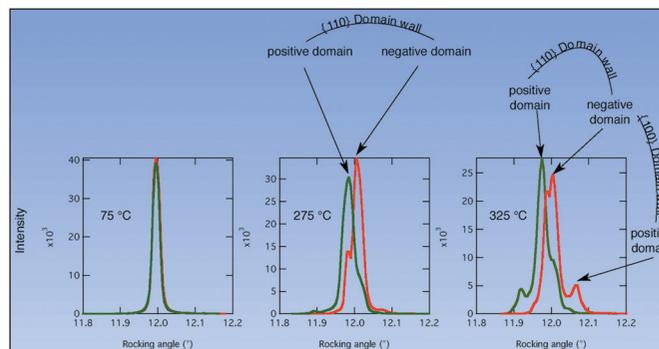


Figure 5: Rocking curves of LaAlO_3 as a function of temperature, showing changes upon maximum (red) and minimum (green) applied stress.

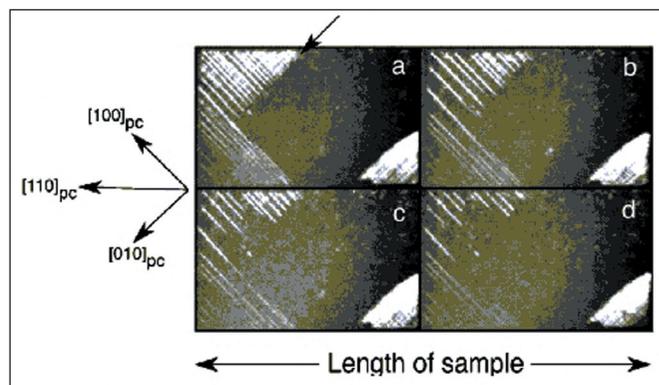


Figure 6: Snapshots of the microstructure of LaAlO_3 under applied force at different stages of the dynamic force cycle for a sample held at 190 °C. (a) A comb of needle twins with walls parallel to the pseudo cubic (010) planes is visible in the upper and lower left corners. The sharp termination of the comb of needles, (arrowed), is caused by the presence of twins which belong to an incompatible chevron orientation. Increasing the applied force causes

retraction of the needles (b) and (c). There is a wide range of tip mobility, so that even at the maximum of the applied force (d) some needles remain unmoved. For movies of these microstructures see: <http://www.esc.cam.ac.uk/astaff/redfern/domains.html>

mechanical analysis. In particular, we anticipate that the anelastic behaviour of polymers could be probed simultaneous with texture measurements from diffraction with a minor modification of the XRD-DMA technique.

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