Detwinning Cell for High-Transition-Temperature Atmosphere-Sensitive Ferroelastic Crystals

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Abstract
A universal cell is reported for detwinning ferroelastic crystals, with transition temperatures that range from 300 to 1300 K, in a controlled atmosphere. A carefully oriented compressive stress on the order of 0.1-1 MN m⁻² is applied to the twinned crystal at room temperature. The crystal temperature is raised from 300 K through the phase transition and is slowly lowered again under stress. The cell has been used to detwin crystals of Na₅W₃O₈F₅ with a Curie temperature of 800 K in an atmosphere of flowing high-purity oxygen, and crystals of Rb₂KMoO₃F₃ with a Curie temperature of 328 K in air. Successful detwinning is demonstrable by the complete conversion of high-angle multiple-component line profiles diffracted by the as-grown crystal to single-component reflection profiles.

Introduction
Ferroelastic crystals grown from the paraelastic phase stable at higher temperatures generally contain mechanical twins. Twin-free material is a prerequisite for the measurement of crystal tensor properties. It is possible to eliminate all ferroelastic twins in a crystal by the application of an appropriately directed compressive stress, provided this is greater than the coercive stress and less than that corresponding to the cohesive strength (Abrahams, 1971, 1979). In the present paper, a universal cell is reported in which ferroelastic crystals with transition temperatures ranging from 300 to 1300 K can be detwinned in a controlled atmosphere. Two examples are presented of microtwinned ferroelastic crystals that have repeatedly been detwinned: one is a material that hydrolyzes rapidly near the transition temperature of 800 K in the presence even of minute concentrations of water vapor, the other is stable in air at the transition temperature of 328 K.

Cell design considerations
The coercive stress of a ferroelastic crystal, namely the minimum stress required to reorient the crystal lattice, may exceed the crystalline cohesive strength at a given temperature. The coercive stress approaches zero at the transition to the paraelastic phase whereas the cohesive strength is often largely temperature independent except in the range close to melting. A twin-free ferroelastic crystal is hence most readily prepared by applying a small compressive stress above the transition temperature and cooling under load. The

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direction of the applied stress is governed by the symmetry change at the phase transition and by the nature of the distortions from the higher symmetry unit cell in the ferroelastic phase. For example, consider a transition from cubic to tetragonal symmetry: if the resulting ratio \(c/a\) is less than unity, twins with \(c\)-axis direction normal to a given cubic axis may be eliminated by applying compressive stress along that axis. In case \(c/a > 1\), detwinning requires the application of compressive stress along a cubic \([110]\).

A universal detwinning cell, based on the considerations above, is shown in cross section in Fig. 1. The twinned crystal plate \(A\) is supported by two gold shim plates \(B\). The purpose of screw \(C\) is to maintain the crystal and supporting plates in the vertical plane: zero pressure is transmitted to the crystal by the screw. The crystal and shim plates occupy a slot milled in the gold cylinder \(D\). The slot is longer than the support and crystal assembly. A gold piston \(E\) rests on the upper surface of the crystal: the piston is set in a stainless steel cylinder of mass 65 g. For a crystal with upper and lower plane parallel surfaces typically with an area of 0.5-5 mm\(^2\), the resulting compressive stress is on the order of 0.1-1 MN m\(^{-2}\). The crystal surfaces in contact with the piston and cylinder are ground normal (within a tolerance of about 2°) to the required stress-detwinning direction.

It may be noted that the minimum compressive stress for detwinning (or ferroelastic reorientation) at the transition temperature is infinitesimally greater than zero, in the absence of pinning defects. Hence, a constant stress on the order of MN m\(^{-2}\) is fully adequate to detwin a normal ferroelastic crystal by this method.

Temperature and atmosphere control

The furnace used with the detwinning cell is of the muffle type, capable of reaching 1700 K, with internal dimensions of 0.19 \(\times\) 0.23 \(\times\) 0.43 m. The stress cell (see above section) is sealed within a quartz jacket, shown diagrammatically in Fig. 2. With the thermocouple bead \(B\) close to the stress cell \(A\), the Pt and 10% Rh, Pt thermocouple leads are passed through the 0.75 m arms \(C\) to a Leeds and Northrup temperature controller. The arms are supported on fire-brick at the furnace mouth, which is effectively sealed with packed spun-ceramic fiber.

The procedure used for hydrolyzable crystals is to connect a supply of ultra-dry high-purity oxygen, containing less water than 2 parts in 10\(^6\), to one arm and to regulate the exit flow to 1.51 min\(^{-1}\). Cell \(A\) is thoroughly flushed before the furnace is energized. With no interruption in the oxygen flow the cell temperature is raised to 50 K above the phase transition, maintained for one hour, and then lowered at 0.5 K min\(^{-1}\) through the Curie temperature and thereafter at 1 K min\(^{-1}\) to room temperature.

The maximum temperature attainable with the quartz jacket before softening occurs is 1300 K. A ceramic jacket would permit higher temperatures to be reached. Substitution of other atmospheres for pure oxygen is trivially simple.

Detwinning of \(\text{Na}_3\text{W}_2\text{O}_5\text{F}_5\) and \(\text{Rb}_2\text{KMoO}_3\text{F}_3\)

Crystals of \(\text{Na}_3\text{W}_2\text{O}_5\text{F}_5\) grown from the melt (Ravez, Elaatmani & Chaminade, 1979) are invariably microtwinned. X-ray powder photography and dielectric permittivity measurements are suggestive of ferroelastic and ferroelectric behavior (Doumerc, Elaatmani, Ravez, Pouchard & Hagenmuller, 1979). Two parallel faces, both about 0.6 mm\(^2\) in area, were ground on an as-grown crystal between 5 and 10° from the normal to a 7.36 Å monoclinic twinned \(a,c\) axis and within 2° of (010). Following a light etch, the profile of the combined 800,008 reflection was measured on a spectrometer with unfiltered Cu K radiation. The divergence of the incident beam was 48°. The resulting \(\alpha_1, \alpha_2\) profile is shown in Fig. 3. Both 800 and 008 components are readily seen.

After utilizing the detwinning procedure of the previous sections, the profile of the same reflection was again measured with results as shown in Fig. 4. One component only is evidently present. The lattice constants of the single domain crystal are: \(a = 7.3620(6)\), \(b = 10.6345(22)\), \(c = 7.3620(8)\) Å, \(\beta = 90.82(2)°\) at 298 K (Ravez, Elaatmani, Hagenmuller & Abrahams, 1981). It may be noted that attempts to detwin an as-grown crystal by applying compressive stress along a twinned 10-485, 10-342 Å assumed-orthorhombic \(a,c\) axis as the crystal was cooled through the phase transition were
not successful. Elimination of the orthorhombic-symmetry possibility by means of this experiment led to selection of the direction in monoclinic symmetry indicated above for efficient detwinning. The reorientation of one twin component in the monoclinic lattice is hence from $180^\circ - \beta$ to $\beta$ under compressive stress. 

Crystals of Rb$_2$KMoO$_4$F$_3$ grown by the Bridgman technique from polycrystalline material prepared by the method of Peraudeau, Ravez & Arend (1978) are almost always microtwinned in the room-temperature rhombohedral phase (Abrahams, Bernstein & Ravez, 1981). Plane parallel (111) faces, with respect to the cubic paraelastic phase, of area close to 10 mm$^2$ were ground on several samples and etched. The resulting profile of the 444 reflection, based on cubic axes, invariably contains a double component at room temperature corresponding to the rhombohedral 40.4 and 00.12 reflections, similar to that shown in Fig. 3. Compressive stress applied along the cubic [110] direction produces components along three of the four cubic space diagonals, with zero component along the fourth.

The loaded detwinning cell with [110] stress applied to the crystal is then heated in a drying oven to 378 K and slowly cooled through the transition to room temperature. The resulting cubic 444 reflection thereupon becomes as single at 300 K as that shown in Fig. 4, and corresponds entirely to the rhombohedral 00.12 reflection. The rhombohedral lattice constants, in hexagonal coordinates, are $a=6.3096(1)$, $c=15.4650(3)$ Å at 300 K and, at the phase transition, become equivalent to the cubic $a/\sqrt{2}$ and $a\sqrt{3}$ spacings respectively.

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References