***Supplementary Materials***

***for***

**Nanoindentation pop-in in oxides at room temperature: dislocation activation or crack formation?**

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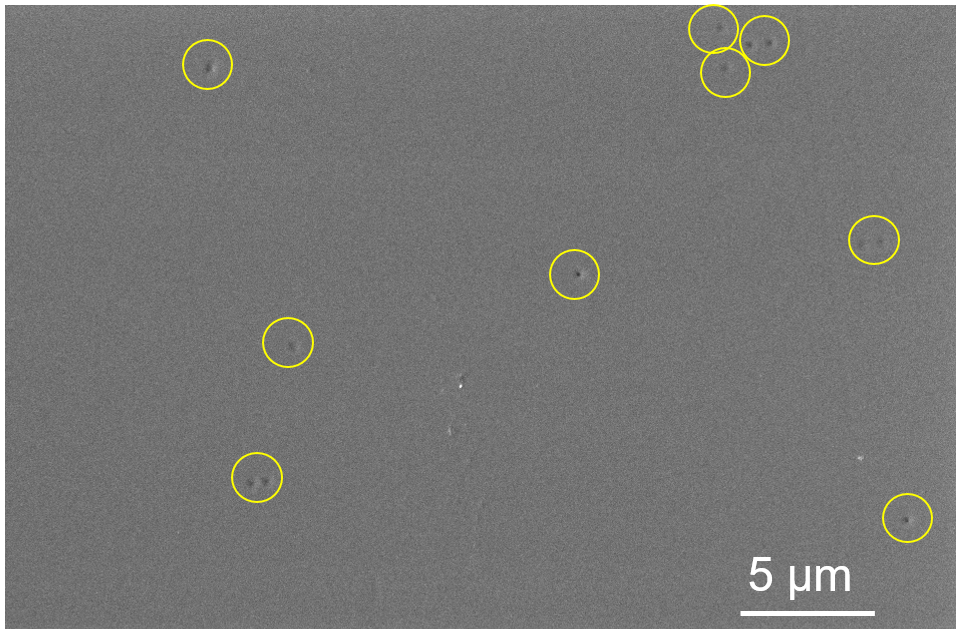
1. Pre-existing dislocation density checked using etch pit for single-crystal SrTiO3

2. Sample information and surface characterization of Al2O3, BaTiO3, and TiO2

3. Deformation results and representative load-displacement curves from indentation pop-in stop tests of Al2O3, BaTiO3, and TiO2

**1. Pre-existing dislocation density in SrTiO3**

The pre-existing dislocation density is revealed by chemical etching, which gives a dislocation density of ~1010 m-2.



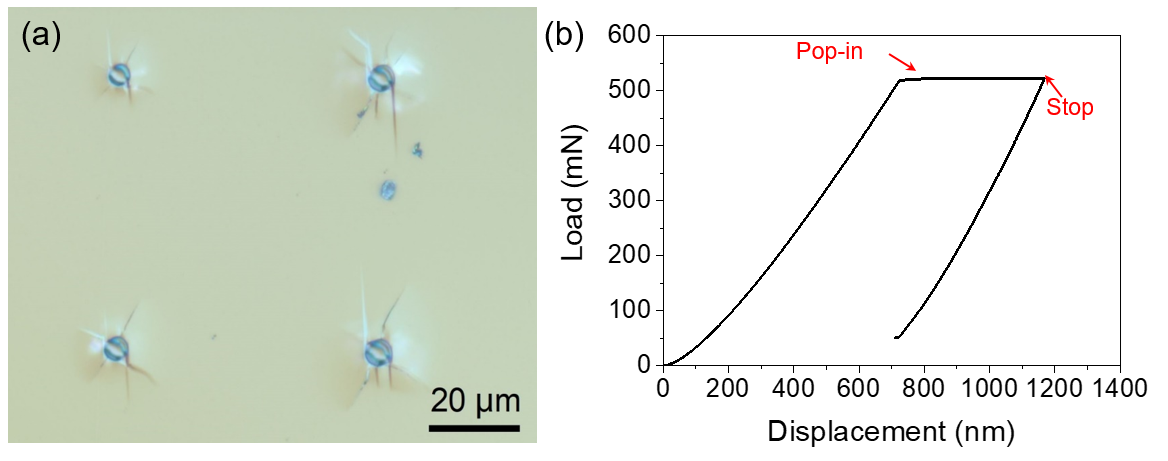
**Fig. S1.** SEM image showing the pre-existing dislocation in SrTiO3 checked using etch pit study. The tiny black dots highlighted by the yellow circles correspond to the pre-existing dislocations.

**2. Sample preparation and characterization of Al2O3, BaTiO3, and TiO2**

The single-crystal alpha-Al2O3 (sapphire) sample with (0001) surface was used. The ferroelectric tetragonal BaTiO3 single crystal (FEE GmbH, a division of EOT, Idar-Oberstein, Germany) was grown with the top-seeded solution growth method and the (001) surface was indented. Prior to indentation test, the ferroelectric BaTiO3 sample was electrically poled at 1 kV/mm to gain a defined spontaneous polarization orientation (out-of-plane). Tests on rutile TiO2 single crystals (CrysTech GmbH, Berlin, Germany) were directly carried out on the (001) polished surface (as-received sample). The characterization of indents traces in the TiO2 sample was carried out with ECCI through a backscatter electron (BSE) detector in a Zeiss Merlin SEM. A beam current of 2 nA, acceleration voltages of 30 kV, and a working distance of 7.5 mm. In order to capture the surface dislocations on BaTiO3, ECCI (MIRA3-XM SEM, TESCAN, Brno, Czech Republic) measurement was performed with an accelerating voltage of 20 kV and a beam current of 500 to 600 pA. Furthermore, in order to minimize the surface damage during sample preparation on the pop-in study, the sample surfaces were all finally polished using vibrational polishing with colloidal silica to remove the surface mechanical deformation layer, similar to the case in SrTiO3.

**3. Deformation results and representative load-displacement curves from indentation pop-in stop tests of Al2O3, BaTiO3, and TiO2**

***3.1 Single crystal α*-*Al2O3***



**Fig. S2**  (a) Optical microscope image showing cracks initiated right after the pop-in stop test on sapphire with *R* = 5 μm; (b) Representative load-displacement curve for Al2O3 with the tip radius of *R* = 5 μm, demonstrating the pop-in stop test.

For indentation on Al2O3, the previous work by Page et al. [[1](#_ENREF_1)] showed that only dislocations were activated the surface was indented with Berkovich tip at a very low load (e.g., corresponding to a maximum indentation depth of 250 nm), as revealed by the TEM image in their work. Unlike the widely extended dislocation arms in SrTiO3, the dislocations shown by Page et al. [[1](#_ENREF_1)] are confined in a very limited region near the indent imprint, suggesting a much higher lattice friction stress inAl2O3, as suggested by the Peierls stress analysis by Kamimura et al. [[2](#_ENREF_2)]. The extremely high lattice friction stress greatly limits the dislocation motion and thus plastic deformation. In addition, the limited slip systems in oxides further facilitates dislocation pileups. Such dislocation pileups could further activate crack initiation based on the Zener-Stroh theory [[3](#_ENREF_3), [4](#_ENREF_4)]. In comparison, the lattice friction stress of SrTiO3 has been reported to be less than 100 MPa [[5](#_ENREF_5), [6](#_ENREF_6)], which is a very low value for an oxide material.

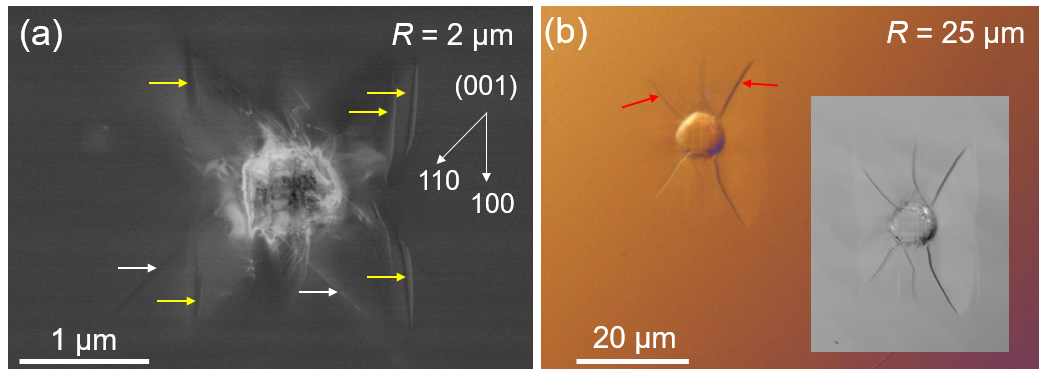
This indentation result by Page et al. [[1](#_ENREF_1)] is consistent with the *in situ* TEM indentation study by Miao et al. [[7](#_ENREF_7)], who recently showed that only dislocations without cracks formation were induced when a sharp tip was indented into the surface of a single crystal Al2O3. On the other hand, it is understandable that crack occurs when *in situ* TEM indentation was performed at the grain boundary of a bi-crystal Al2O3 due to the weak bonding at the grain boundary, as reported by Kondo et al. [[8](#_ENREF_8)].

In contrast, cracks start to initiate right after the pop-in stop test with *R* = 5 μm. The irregular pattern of the cracks in Fig. S2a indicates a stochastic behavior of the crack formation, which is probably due to: i) the stochastic distribution of the pre-existing flaws/cracks; ii) the instable dynamic crack propagation coupled with the machine dynamics during pop-in event [[9](#_ENREF_9)].

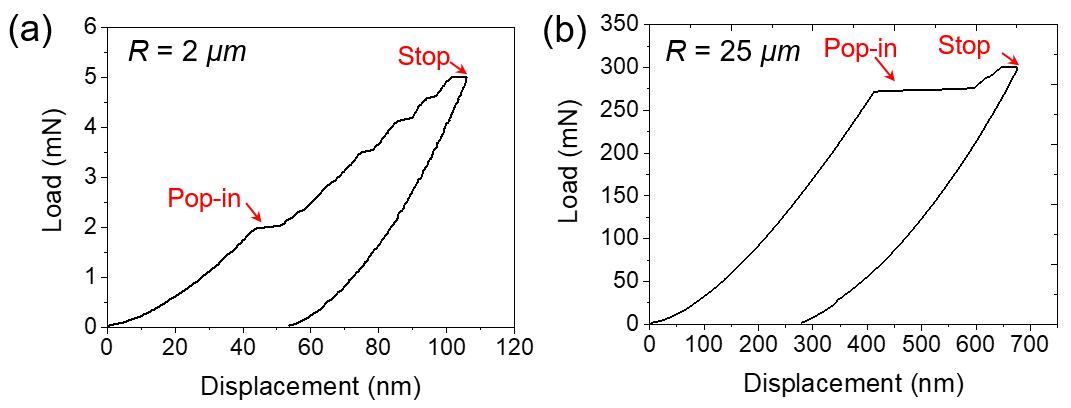
***3.2 Single crystal BaTiO3***

As the evidence of dislocations under Berkovich tip has been found above in SrTiO3 and α-Al2O3, here we perform directly spherical indentation with *R* = 2 μm and *R* = 25 μm in one domain on the (001) surface of a single crystal BaTiO3. Similarly, the indentation were stopped right after the pop-in events to prevent local materials from being further deformed. Figure. S3 clearly demonstrated the indentation size effect on the material deformation behavior. The ECCI measurement on an indent imprint with *R* = 2 μm in Fig. S3(a) features the dislocations (white lines with tails around the indenter imprint) and some domain structures (yellow arrows) induced by local high stress, while no cracks were visible. The white arrows indicate representatively the indentation induced slip patterns, which agree with the room-temperature slip system {110}<110> in BaTiO3 [[10](#_ENREF_10)].

In contrast, the light microscope for an indent imprint with tip radius *R* = 25 μm in Fig. S3b shows clearly the crack formation right after pop-in. The crack pattern seems irregular and does not follow a specific plane as the crack pattern and length in ferroelectric materials can be modified with the ferroelectric domain structure [[11](#_ENREF_11)]. The exact underlying mechanisms for crack formation can be complex [[12](#_ENREF_12)] and are beyond the scope of this work. To eliminate a strong influence of the domain patterns, the sample was electrically poled.



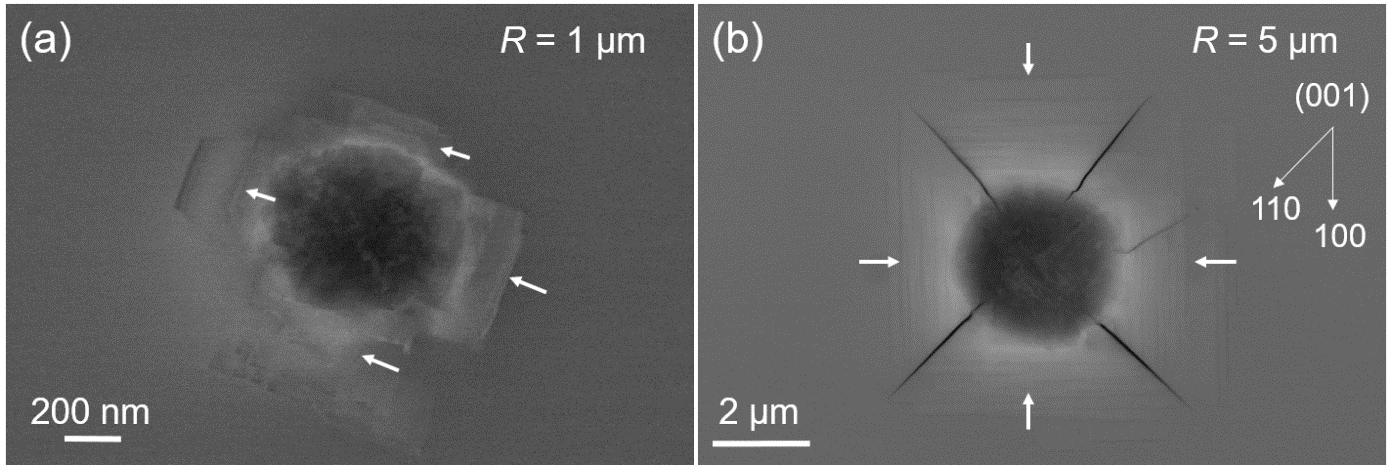
**Fig. S3** Images taken on indented regions where pop-in stop tests were carried out: (a) ECCI measurement shows numerous dislocations without a crack in the indented region with 2 μm spherical tip. The white arrows indicate the slip planes, the yellow arrows indicate the domain structures induced by local stress; (b) optical image with differential interference contrast mode showing cracks under 25 μm spherical tip. The red arrows indicate the cracks. The inset image shows the corresponding location observed by a laser microscope.



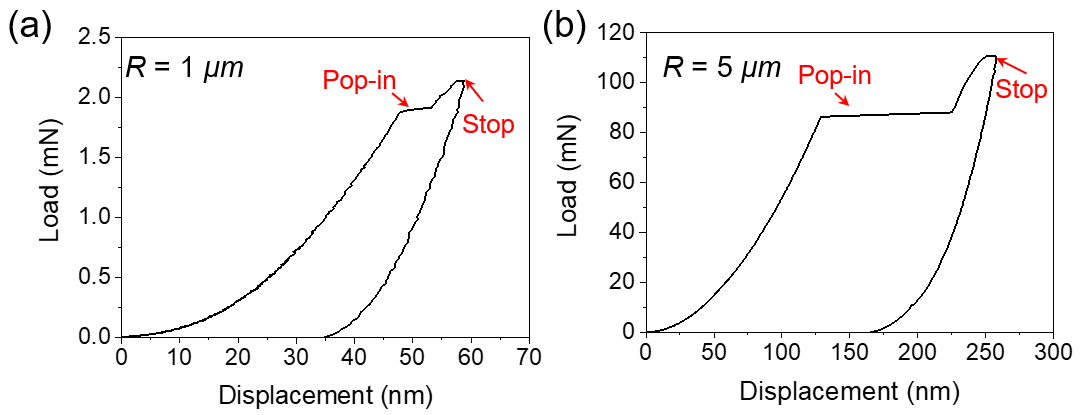
**Fig. S4** Representative load-displacement curves for BaTiO3 with different tip radii, demonstrating the pop-in stop tests.

Gaillard et al. [[10](#_ENREF_10)] performed indentation using Berkovich tip up to a load of 22 mN on (001) surface of BaTiO3 and used AFM to characterize the surface morphology. It was demonstrated that the deformation is accommodated by mechanical twinning and domain switching. Here in Fig. S3a, the ECCI result shows direct evidence of the dislocations without crack formation. The slip patterns revealed by ECCI resembles that by AFM on (001) BaTiO3 after indentation with 1 μm (± 0.2 μm) spherical tip by Liu et al. [[13](#_ENREF_13)].

***3.3 Single crystal TiO2***



**Fig. S5** Images taken on indented regions on (001) TiO2 where pop-in stop tests were carried out: (a) ECCI measurement showing no crack induced but features of (partial) dislocations which are not yet developed to twins [[14](#_ENREF_14)] in the indented region and pileups (white arrows) with *R* = 1 μm; (b) ECCI measurement showing cracks initiated mainly on (110) planes, together with slip lines (white arrows) on all four  systems with *R* = 5 μm.



**Fig. S6** Representative load-displacement curves for TiO2 with different tip radii, demonstrating the pop-in stop tests.

The ECCI observation in Fig. S5 shows again compelling evidence that small tip (*R* = 1 μm, Fig. S5a) induces plastic deformation dominated by dislocations, while larger tip (*R* = 5 μm, Fig. S5b) induced both slips and crack formation during the pop-in. The pileup pattern around the indent imprint is analogous to that of a single-crystal Si after indentation [[15](#_ENREF_15)]. The slip and crack patterns in Fig. S5b resemble the results by Ashbee et al. [[16](#_ENREF_16)] using a pyramid diamond tip in air at room temperature.

**Table S1** Summary of the maximum shear stress and maximum tensile stress under the smallest tip (without inducing cracks at pop-in) used for corresponding oxides and theoretical shear strength and fracture strength. The comparison shows that the maximum shear stress is reached much more easily before the maximum tensile stress, so that dislocation nucleation is more strongly favored.

|  |  |  |  |
| --- | --- | --- | --- |
|  | Al2O3  (Berkovich [[1](#_ENREF_1)]) | BaTiO3  (Spherical, *R* = 2 μm) | TiO2  (Spherical, *R* = 1 μm) |
| Young’s modulus, E (GPa | 390 [[1](#_ENREF_1)] | ~120 [[17](#_ENREF_17)] | ~349 [[18](#_ENREF_18)] |
| Poission’s ratio | 0.25 [[1](#_ENREF_1)] | 0.3 [[17](#_ENREF_17)] | 0.25 [[18](#_ENREF_18)] |
| Shear modulus, G (GPa) | ~156 | ~55 [[13](#_ENREF_13)] | ~140 |
| Theo. shear strength (G/2π, GPa) | ~24 | ~9 | ~22 |
| Theo. fracture strength (E/10, GPa) | ~37 | ~14 | ~35 |
| Pop-in load (mN) | ~7 [[1](#_ENREF_1)] | 2.0 | 1.9 |
| Max. shear stress (GPa) | ~8.5 [[1](#_ENREF_1)] | ~3.8 | ~9.5 |
| Max. tensile stress (GPa) | ~3.6 | ~1.6 | ~4.1 |

*\*Note the calculation of the max. shear stress and max. tensile stress is made according to Eq. (3) and Eq. (5) in the main text. The relation between shear modulus, Young’s modulus, and Poisson’s ratio is estimated by G=E/2(1+v) for isotropic behavior for simplicity. The value may differ slightly from the bulk values.*

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