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RAPID COMMUNICATION

Mechanical tailoring of dislocation densities in $SrTiO_3$ at room temperature

Chukwudalu Okafor | **Kuan Ding** | **Xiandong Zhou** | **Karsten Durst** | **Jürgen Rödel** | **Xufei Fang**

Department of Materials and Earth Sciences, Technical University of Darmstadt, Darmstadt, Germany

Correspondence
Xufei Fang, Department of Materials and Earth Sciences, Technical University of Darmstadt, 64287 Darmstadt, Germany.
Email: fang@ceramics.tu-darmstadt.de

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Abstract

Dislocation-tuned functional properties such as electrical conductivity, thermal conductivity, and ferroelectric properties in oxides are attracting increasing research interest. A prerequisite for harvesting these functional properties in oxides requires successful introduction and control of dislocation density and arrangement without forming cracks, which is a great challenge due to their brittle nature. Here, we report a simple method to mechanically tailor the dislocation densities in single-crystal perovskite $SrTiO_3$. By using a millimeter-sized Brinell indenter, dislocation densities from $\sim 10^{10}$ to $\sim 10^{13}$ m^{-2} are achieved by increasing the number of indenting cycles. Depending on tip radius and indenting load, large and crack-free plastic zones over hundreds of micrometers are created. The dislocation multiplication mechanisms are discussed, and the work hardening in the plastic zone is evaluated by micro-hardness measurement as a function of dislocation density. This simple approach opens many new opportunities in the area of dislocation-tuned functional and mechanical studies.

KEYWORDS

cyclic loading, dislocations, hardness, strontium titanate

1 | INTRODUCTION

Recently, dislocations have been introduced into ceramics for the mechanical purpose to improve plasticity[1] and fracture toughness[2,3] but also have demonstrated great potential in tuning electrical conductivity,[4] thermal conductivity,[5] dielectric, and piezoelectric properties.[6] A key prerequisite for harvesting these properties is the manipulation of dislocation densities and arrangement in ceramics.[7,8] Methods to introduce dislocations into ceramics include but are not limited to flash sintering,[9] bicrystal bonding,[10] thin film deposition,[11] surface grinding,[2] and mechanical deformation.[12,13] The advantages and limitations of these methods have been briefly discussed elsewhere by the current authors.[14]

Here, we focus on the mechanical deformation using the cyclic indentation method with a large Brinell indenter at room temperature on single-crystal $SrTiO_3$ (STO), which is a perovskite that has been extensively studied for dislocation-tuned functionalities.[7] This method has the potential to provide high dislocation densities at suitable volumes for functional evaluation.

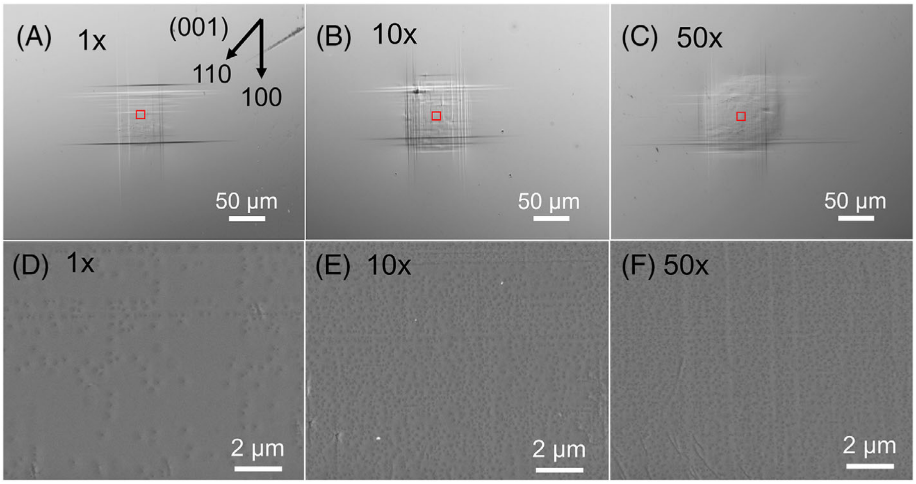

FIGURE 1 Plastic zone and corresponding dislocation etch pit patterns after cyclic loading with the optimized load (1.5 kg) for different cycles: (A, D) 1x, (B, E) 10x, and (C, F) 50x. Note (A–C) are optical images, and (D–F) are scanning electron microscope (SEM) images taken in the center of the plastic zone (red rectangles)

2 | EXPERIMENTAL PROCEDURE

Un-doped, single-crystal STO samples (Alineason Materials Technology GmbH, Frankfurt am Main, Germany) were used for tests (see Supporting Information Section 1 for details) on a universal hardness testing machine (Karl-Frank GmbH, Weinheim-Birkenau, Germany) mounted with a Brinell indenter. A stainless steel indenter with a tip diameter of 2.5 mm was used for the cyclic loading. The micro-hardness within the plastic zone generated by the Brinell indenter was quantified with the Vickers hardness tester (Zwick Roell GmbH & Co. KG, Ulm, Germany).

The surface slip traces after deformation were visualized using optical microscopy (Zeiss Axio Imager2; Carl Zeiss AG, Oberkochen, Germany) in the circularly polarized light–differential interference contrast mode, which enhances the surface features with high resolution and high contrast. The obtained images were consistently post-processed and presented as grey-scale images. The dislocation densities and etch pit patterns in the plastic zone were characterized using a scanning electron microscope (SEM, TESCAN MIRA3-XMH; Brno, Czech Republic) and a laser confocal microscope (LEXT OLS4100; Olympus IMS, Waltham, USA) after surface etching.[15,16]

3 | RESULTS AND DISCUSSIONS

Based on the optimization of load and cyclic number (Figures S1 and S2), we chose the load of 1.5 kg for further investigation of the cyclic loading on the dislocation density in the following section. Figure 1A–C features the representative optical images from 1, 10, and 50x loading. An increase in the plastic zone size is evident from 1x to 10x, but slightly afterward up to 50x. The horizontal and vertical slip lines correspond to the intersection of the {110} slip planes with the (001) surface.[15] Here, four equivalent slip planes $(\bar{1}01)$, (101), $(0\bar{1}1)$, and (011) with a 45° inclination to the indented surface are activated.[17] The stress analysis and activation of the planes are given in Figures S3 and S4. Correspondingly, the dislocation densities in the center region of the plastic zones after 1, 10, and 50x loading are presented in Figure 1D–F. The reference sample (Figure S5) has a dislocation density of $\sim 10^{10}$ m^{-2}. After 1x indentation, the dislocation density increased to $\sim 10^{11}$–10^{12} m^{-2}, but with a rather discrete and scattered distribution of the etch pits in a horizontal and vertical arrangement (Figure 1D). Further increase of the number of cycles to 10x (Figure 1E) leads to an almost uniform and dense distribution of the dislocation etch pits, which is similar to that for 50x (Figure 1F). The saturated dislocation density is found to be of the order of $\sim 10^{13}$ m^{-2} with a plastic zone size of ~ 200 μm.

Note that the spatial distribution analysis of dislocations suggests an almost constant dislocation density within the plastic zone. Figure 2 features a representative indent with 35x cycles with a 1.5 kg load. We estimated the dislocation density from the center (position 1 in Figure 2A) to the peripheral region (position 6 in Figure 2A) due to the symmetry of the indent imprint. An overview of the dislocation densities for 5, 20, and 35x is illustrated in Figure 2C. The close resemblance of the spatial distribution of dislocation densities for 20 and 35x cycles in Figure 2C confirms the saturation of dislocation densities ($\sim 1.4 \times 10^{13}$ m^{-2} approaching the center of the plastic zone), which is consistent with the results in Figure 1E,F. In contrast, the indent with 5x reveals a lower dislocation density ($\sim 3 \times 10^{12}$ m^{-2} in the center). All three curves (Figure 2C) and the SEM image (Figure 2B) demonstrate a relatively

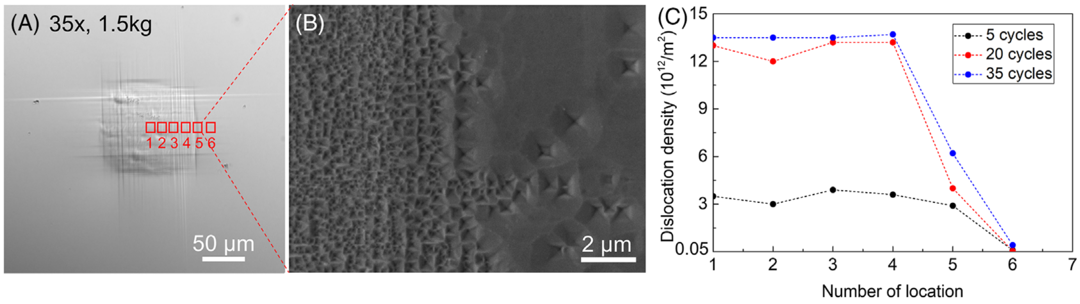

FIGURE 2 Spatial distribution of dislocation density from the center of the plastic zone to the outer region: (A) an example of the plastic zone after 35x cycles of loading with 1.5 kg, (B) scanning electron microscope (SEM) image illustrating the etch pits for position 5 in (A), and (C) dislocation density as a function of the location for different numbers of cycles (5, 20, and 35x)

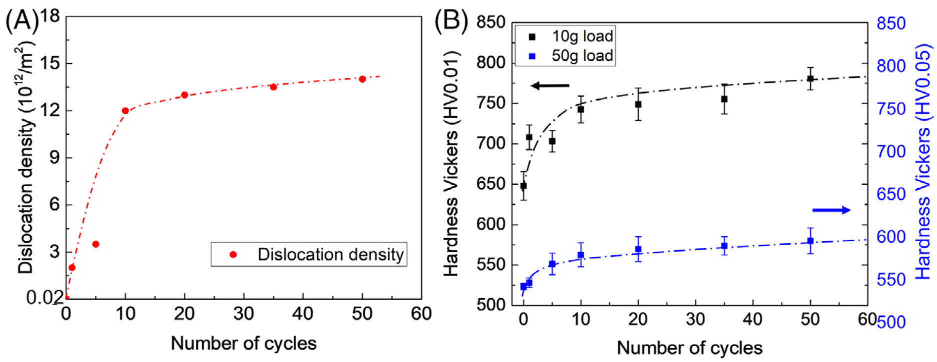

FIGURE 3 (A) Plot of dislocation density in the center of the plastic zone as a function of the number of cycles with 1.5 kg load and (B) Vickers micro-hardness for two different loads (10 and 50 g) in the plastic zones after a different number of cycles. The error bars are calculated for at least eight indents for each condition

sharp transition from a dislocation-rich region (inside plastic zone) to a dislocation-poor region (outside plastic zone).

The increase of the dislocation density as a function of an increased number of cycles is attributed to dislocation multiplication mechanisms. Johnston and Gilman[18] provided compelling experimental evidence for dislocation multiplication in single-crystal LiF, which has a cubic structure and the same slip systems as in STO. The multiplication of the dislocations on each single slip plane can be dominated by Frank-Read sources,[19,20] while the widening of the slip bands (see multiple parallel slip traces in Figure S4) is suggested to be dominated governed by cross slip. The etch pits revealed in the vertical and horizontal <100> directions correspond to the screw components considering the 3D construction of the dislocations underneath the indenter for STO,[15,16] which suggests that the cross slip of screw dislocations is responsible for the multiplication process.[18] Further possible contributions to the multiplication could be attributed to the generation of numerous immobile dislocation components[21] as well as the debris[2] during the cyclic loading.

The impact of various dislocation densities on the microhardness is further evaluated using Vickers hardness. The corresponding Vickers hardness values (HV0.01 for 10 g load and HV0.05 for 50 g load) as a function of the dislocation densities (accordingly, number of cycles according to Figure 3A) are summarized in Figure 3B. Two features are evident: i) for both loads, the hardness values consistently increase as the dislocation density increases, approaching a plateau after about 10x cycles; ii) the lower load (10 g) yields a relatively higher hardness value at given dislocation density, which can be rationalized by the indentation size effect.[22] The change of hardness as a function of dislocation density agrees with Brookes et al.[23] who developed a cyclic scratch method to increase the dislocation density in single-crystal MgO and found a saturation of the (Knoop) hardness after about 10 to 20 cyclic wear tests. The direct correlation between hardness and dislocation density as a function of indentation cycles suggests dislocation work hardening in STO, akin to that reported in MgO.[23]

4 | CONCLUSION

A simple experimental method using large spherical indentation and cyclic loading is demonstrated on single-crystal (001) $SrTiO_3$ to tune dislocation densities over three orders of magnitude in a large plastic zone (hundreds of micrometers) without the formation of cracks. After about 10 cycles of repetitive indentation on the same location, a saturation of dislocation density inside the plastic zone is identified to be higher than 10^{13} m^{-2}. Dislocation multiplication mechanisms, including both Frank-Read sources and Koehler sources (cross slip), are suggested to operate to increase the dislocation densities. Work hardening is evidenced by the microhardness increase as a function of dislocation densities. This simple technique guarantees large plastic volumes with high dislocation densities for future assessment of dislocation-tuned functional properties. The simplicity of this experimental approach merits its application for other room-temperature "ductile" ceramics, as well as for various structural ceramics if this method is driven to high temperature.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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SUPPORTING INFORMATION

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