

Revealing the atomic-scale structures of dislocations in calcium fluoride single crystal

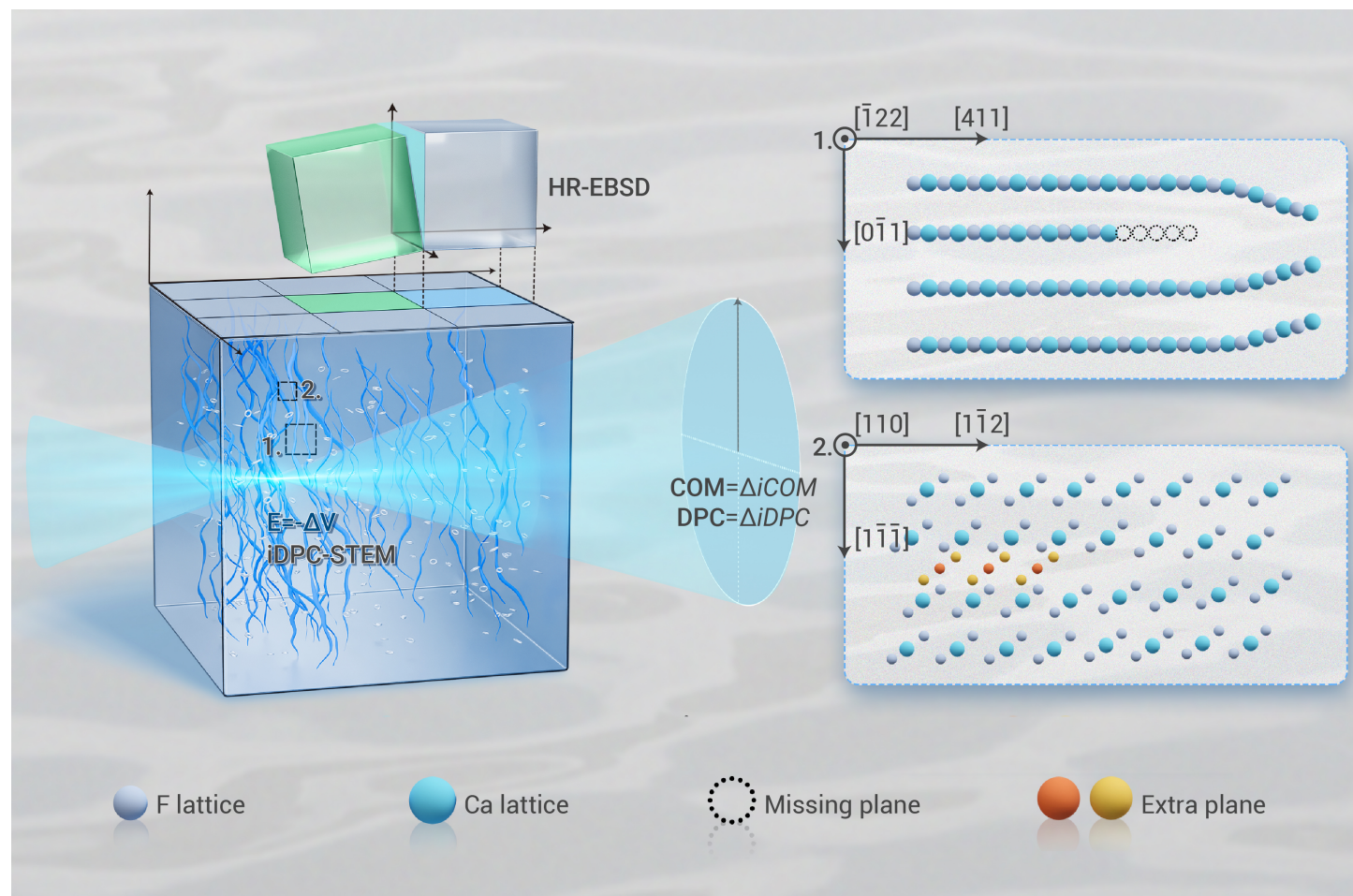
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GRAPHICAL ABSTRACT



PUBLIC SUMMARY

- The atomic structure of dislocations were identified by utilizing a combination of characterization methods.
- The underlying mechanism responsible for dislocation formation is revealed.
- Strategies for suppressing the formation of dislocations are proposed.

Revealing the atomic-scale structures of dislocations in calcium fluoride single crystal

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Dislocations are ubiquitous in crystalline solids and play a critical role in both material properties and device performance. Due to the numerous variables influencing crystal growth, such as temperature, pressure, and impurity levels, the synthesis of high-quality crystals with minimal defects remains a challenging and enduring goal in crystal research. Calcium fluoride (CaF₂) which is widely used in optical devices typically contains dislocations on the order of 10⁻⁵ cm⁻². The sensitivity of the weak CaF₂ lattice to electron beams makes at atomic-level imaging using traditional scanning transmission electron microscopy difficult. Here, we utilize a combination of characterization methods to analyze the microstructure of dislocations in CaF₂, and the existence of both stored statistical dislocations (SSDs) and geometrically necessary dislocations (GNDs) are identified. SSDs mainly consist of perfect dislocations with a small amount of Frank partial dislocations, while GNDs are predominantly composed of Frank partial dislocations and stacking faults. Based on the calculated formation energies of dislocations and fluoride vacancies, the formation mechanisms of SSDs and GNDs are proposed. The findings in the present study deepen our understanding of the dislocations in CaF₂ and offer insights into strategies to further reduce the defect concentration in CaF₂ crystals.

INTRODUCTION

Dislocations are quasi-one-dimensional defects in crystals, characterized by localized atomic disorder. Studies demonstrate that dislocations strongly influence optoelectronic and semiconductor device performance by altering band structures and electron transport properties.¹⁻⁴ Moreover, dislocations serve as charge carrier scattering centers, degrading the conductivity of crystalline devices.⁵⁻⁶ Furthermore, dislocations can significantly alter the crystal's refractive index, adversely affecting optical device imaging quality. Therefore, growing dislocation-free or near-dislocation-free crystals is essential for high-performance electronic and optical applications.⁷⁻⁹ However, dislocations inevitably form during crystal growth due to thermodynamic and kinetic factors, as well as inhomogeneous growth conditions. Consequently, producing near-dislocation-free crystals has emerged as a key research focus. Decades of research have significantly reduced dislocation densities in common electronic and optical materials, including Si, SiC, sapphire, and GaN.¹⁰⁻¹⁴ Notably, single-crystal Si, 4H-SiC, and sapphire now exhibit near-dislocation-free densities—for example, the highest-quality Si achieves dislocation densities as low as 1-10 cm⁻².¹⁰ For 6-inch conductive 4H-SiC substrates, the threading screw dislocation (TSD) density has been reduced to below 200 cm⁻², with high-quality substrates achieving values under 50 cm⁻².¹¹ Furthermore, sapphire crystals grown by the temperature gradient technique (TGT) exhibit dislocation densities as low as ~100 cm⁻² in their optimal regions.¹³ In contrast, CaF₂ single crystals - despite being excellent optical materials - still maintain relatively high dislocation densities, typically in the range of 10⁴ to 10⁵ cm⁻².¹⁵⁻¹⁶ The high dislocation density in CaF₂ single crystals substantially degrades their stress birefringence, optical uniformity, and laser damage threshold. These limitations restrict their use in demanding applications including high-end lithography, space cameras, high-power laser systems, and high-precision optical detection equipment. Consequently, achieving near-dislocation-free CaF₂ crystals through dislocation reduction or suppression has become crucial for fabricating high-performance, low-defect-density optical devices. This imperative has made dislocation prevention in

CaF₂ crystals a prominent research focus.¹⁷⁻²¹

Current research on CaF₂ dislocations primarily focuses on slip systems, dislocation migration, and the morphology of dislocation etch pits. The primary slip system of CaF₂ crystals was identified as {100}/<110> and the secondary slip system as {110}/<110>, using the chemical etch method.⁴ Studies have revealed that the core structure of dislocations serves as the determining factor governing the mobility of both edge and screw dislocations.²² Based on this understanding, investigations into the motion of screw and edge dislocations in CaF₂ single crystals were conducted using optical microscopy and chemical etching methods. It was found that screw dislocations exhibit greater mobility than edge dislocations. In the presence of impurities, both types of dislocations show reduced mobility, with this reduction being more pronounced for screw dislocations than for edge dislocations.²³⁻²⁴ Etching studies have identified two characteristic dislocation distribution patterns in CaF₂: free and regular arrangements. This distinction implies fundamental differences between dislocation types and suggests a potential correlation between dislocation configurations and the formation of grain boundaries or other defect structures in CaF₂ crystals. To deepen our understanding of CaF₂ dislocations, precise characterization of their types and atomic-scale structures is essential. However, current research remains limited to macroscopic observations, with no detailed reports available on the atomic configurations and specific types of dislocations in CaF₂ single crystals. During crystal evolution, dislocations reorganize to minimize system energy, forming dense tangles, dislocation walls, subgrain boundaries, and small-angle grain boundaries. These defects ultimately arrange into ordered planar arrays.²⁷⁻³⁰ Grain boundary structures are classified by misorientation angle into large-angle grain boundaries (>10°), small-angle grain boundaries (<10°), subgrain boundaries (<2°), and dislocation walls (0.5°–0.8°).^{28,31-33} Electron backscatter diffraction (EBSD) has emerged as a powerful technique for microstructural characterization, capable of providing detailed information about grain morphology, crystallographic orientation, and boundary types. However, conventional EBSD systems using Hough transform-based analysis are fundamentally limited to an orientation resolution of 0.5°–1° due to constraints imposed by electron beam parameters and calibration accuracy. This resolution limit becomes particularly significant when studying CaF₂ crystals, where many dislocations exhibit regular arrangements with spacings below 25 nm and corresponding small-angle misorientations under 0.9°, as noted in reference.³⁴ These limitations render conventional EBSD insufficient for precise misorientation characterization of such defects, resulting in an incomplete understanding of their microscopic configurations - including dislocation walls, subgrain boundaries, and small-angle grain boundaries.^{16,25} Recent advances in electron backscatter diffraction (EBSD) have led to the development of high-resolution techniques that analyze Kikuchi band displacements at the pixel level, achieving significantly greater precision than conventional Hough transform-based methods.³⁵ Our laboratory has contributed to this progress through the development of the Line Rotated Remap (LRR) algorithm for high-resolution EBSD. This innovative approach effectively reduces errors associated with large-angle rotations in diffraction patterns, achieving an exceptional orientation precision of 0.06°. Such resolution enables accurate characterization of regular dislocation microstructures and reliable determination of dislocation structure types. While HR-EBSD provides comprehensive crystallographic data - including crystal orientation, grain boundary characteristics, and material quality - it

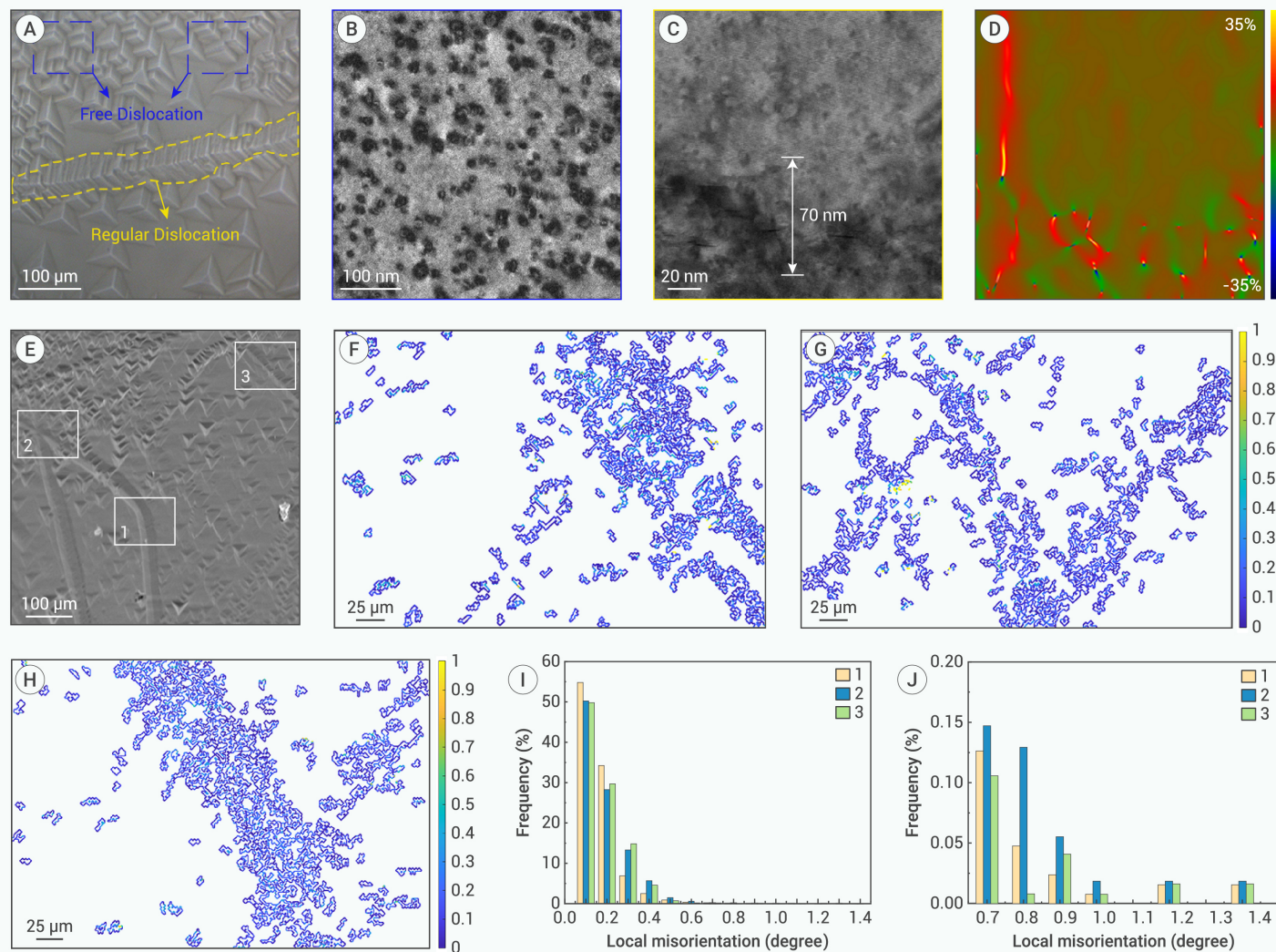


Figure 1. Morphology, Distribution, and Stress Field Analysis of Dislocations in CaF_2 Crystals (A) Dislocation corrosion topography in optical microscope. The blue boxes indicate free dislocations and the area between the yellow dashed lines indicates the regular dislocations. (B, C) Low-magnification iDPC-STEM images of free dislocations and regular dislocations. (D) The GPA of (C), showing the stress distribution. (E) SEM image of dislocation corrosion topography. The white boxes indicate the selected areas for EBSD characterization. (F–H) Distribution map of dislocation misorientation angles corresponding to regions 1–3 in (E). (I, J) Statistical distribution of dislocation misorientation angles. (J) Enlarged distribution of misorientation angles in the range of 0.7 – 1.5° .

remains limited to the mesoscale and cannot resolve the atomic structure of dislocations. Therefore, direct investigation of dislocation core structures at the atomic scale using electron microscopy remains an indispensable component of dislocation research, particularly for definitive identification of dislocation types.

The extreme electron beam sensitivity of CaF_2 single crystals presents a significant challenge for atomic-scale characterization. Under high electron dose conditions, CaF_2 rapidly undergoes structural amorphization,^{36–38} preventing conventional techniques from obtaining atomic-resolution information about dislocations. Recent advances in integrated differential phase contrast scanning transmission electron microscopy (iDPC-STEM) have opened new possibilities for studying such beam-sensitive materials. This cutting-edge technique enables high-resolution imaging at ultra-low electron doses,^{39–41} through the use of multi-zone probes and sophisticated algorithms. iDPC-STEM has proven particularly valuable for characterizing both light and heavy elements in sensitive materials,^{42–43} as demonstrated by its successful application to zeolites, metal-organic frameworks (MOFs), and covalent organic frameworks (COFs).^{44–49} For example, Shen et al. achieved atomic-resolution imaging of single pyridine adsorption configurations in ZSM-5 molecular sieves, marking a breakthrough in atomic-level imaging of single molecules within molecular sieves.⁴⁵ Similarly, Bhattacharjee et al. used iDPC-STEM to observe the structure and evolution of surface interfaces and defects in MIL-101 crystals, revealing stability differences between two

different (111) surface structures.⁴⁶ These advancements suggest that iDPC-STEM could open new possibilities for studying the atomic structure of dislocations in CaF_2 single crystals.

The present work utilizes both the high-resolution EBSD method and the iDPC-STEM technique to characterize the atomic-scale microstructures of dislocations in CaF_2 single crystal. Two types of dislocations and their atomic-scale structures are clearly identified. Combined with the crystal growth process, the formation mechanism of these two types of dislocations is elucidated. The findings in this study through new light on the atomic structures of defects in CaF_2 and laid the foundation for achieving near-dislocation-free in CaF_2 crystals.

MATERIALS AND METHODS

Single crystal preparation

CaF_2 single crystals were grown by utilizing the Vertical Bridgman method with resistance heaters. During the growth process, the vacuum in the crucible was below 10^{-3} Pa, and the growth temperature was set to 1400°C . The grown large-size crystal sample is shown in the Figure S1. All the samples used in this experiment were fabricated from CaF_2 crystals with $\langle 111 \rangle$ orientation through cutting, grinding, and polishing. All crystal faces were polished to optical grade ($R_z < 0.01 \mu\text{m}$) with sample size of $25 \text{ mm} \times 25 \text{ mm} \times 10 \text{ mm}$.

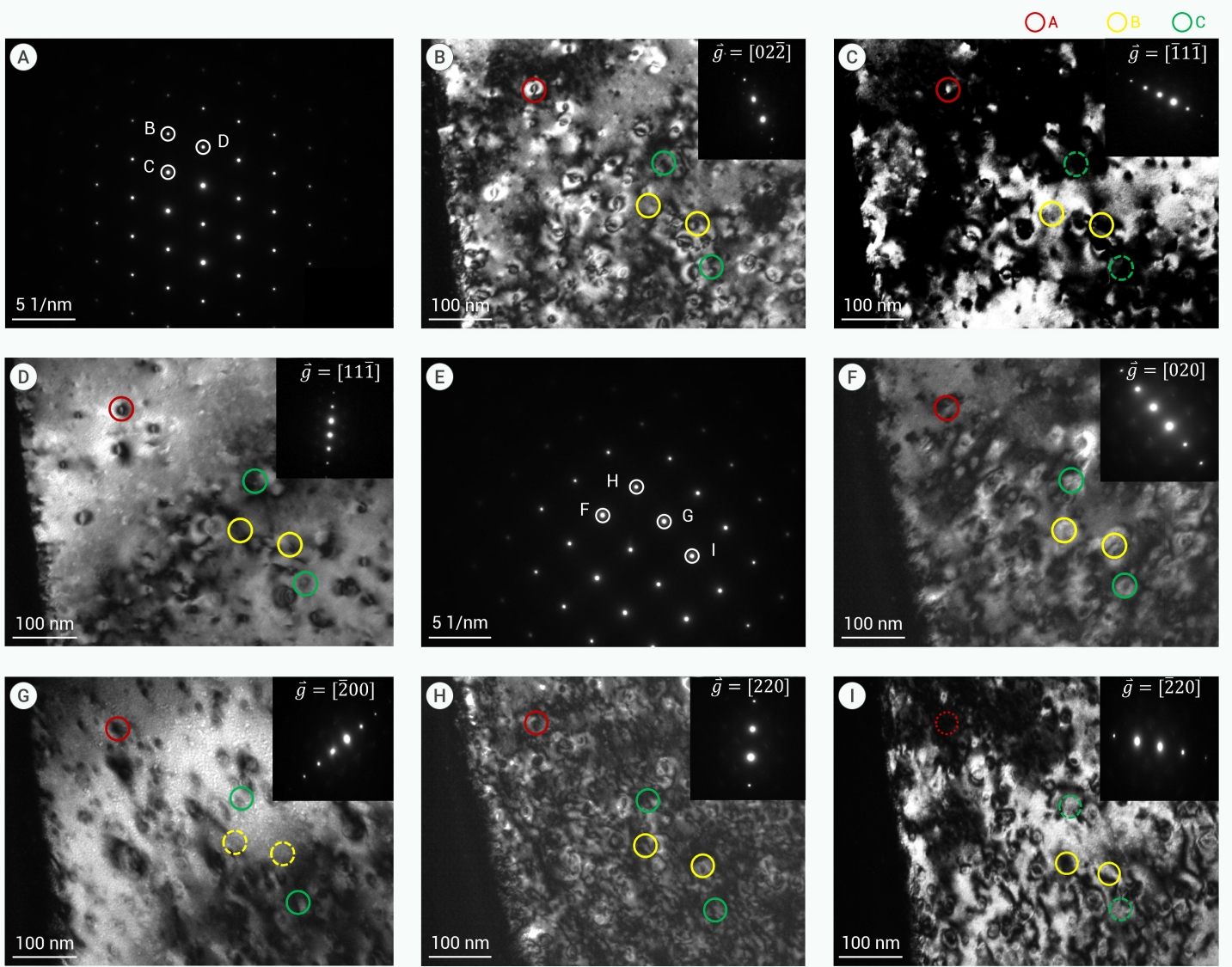


Figure 2. Diffraction Contrast and Defect Imaging of CaF_2 under Multiple Zone Axis and Diffraction Conditions SAED of CaF_2 obtained using two different zone axis: (A) $[011]$ (E) $[001]$ and kinematic dark field images of CaF_2 crystal obtained using two different zone axis and various $\vec{g}$ conditions. (B–D) $[011]$ zone axis: $[02\bar{2}]$, $[\bar{1}1\bar{1}]$, $[11\bar{1}]$. (F–I) $[001]$ zone axis: $[020]$, $[200]$, $[220]$, $[\bar{2}20]$.

Table 1. Burgers vector analysis using $\vec{b} \times \vec{g} = 0$ invisibility criterion.

$\vec{g}$	$[02\bar{2}]$	$[\bar{1}1\bar{1}]$	$[11\bar{1}]$	$[020]$	$[\bar{2}00]$	$[220]$	$[\bar{2}20]$	$\vec{b}$
A	V	V	V	V	V	V	I	$[\bar{1}\bar{1}1]$
B	V	V	V	V	I	V	V	$[0\bar{1}1]$
C	V	I	V	V	V	V	I	$[110]$

Microstructure characterization

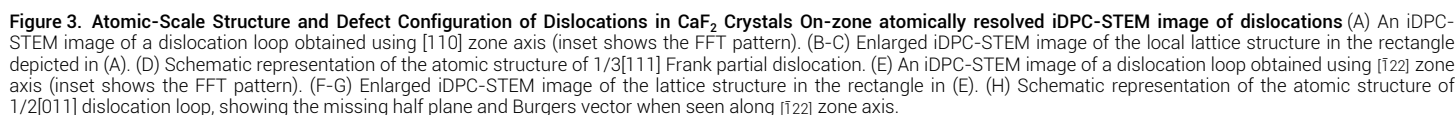
Sample Preparation. Transmission electron microscope samples were prepared using an FEI Versa 3D dual-beam focused ion beam (FIB) microscope. Prior to milling, a protective platinum (Pt) layer was deposited in situ on the sample surface using the FIB's integrated gas injection system. The prepared lamellae were subsequently transferred to TEM copper grids using an ex-situ nanomanipulator lift-out technique.

high-resolution EBSD Characterization. For dislocation misorientation characterization, samples prepared via identical FIB protocols were examined using an FEI Magellan 400 field-emission scanning electron microscope equipped with an Oxford Instruments Nordlys 2 EBSD detector. The diffraction pattern resolution was optimized by configuring the acquisition system in 1×1 binning mode, which maximizes signal fidelity for CaF_2 crystal analysis.

iDPC-STEM Characterization. Following FIB preparation, samples underwent additional low-energy ion milling to remove amorphous surface damage layers. Atomic-scale dislocation analysis was performed using a ThermoFisher Themis Z 300 kV aberration-corrected STEM equipped with dual (probe and image) correctors. The microscope was operated with a convergence semi-angle of 17.8 mrad, and iDPC-STEM images were acquired at a camera length of 285 mm using DF4 detectors with inner and outer collection angles of 5 mrad and 26 mrad, respectively.

Computational details

The first-principles calculations were carried out within the framework of density functional theory (DFT)⁵⁰ as implemented in the Vienna *ab initio* simulation package (VASP) code.^{51–54} The electron-ion interaction is treated



where $E_{\text{tot}}(\text{dislocation})$ and $E_{\text{tot}}(\text{bulk})$ represent the total energy of the super-

The etch pits were initially generated from the corrosion in a mixed solution of hydrochloric acid (37%) and water (volume ratio 1:2) at 333K, and then they were observed using an optical microscopy (see [Figure 1A](#)). The dislocation etch pits exhibited both free dislocations regular dislocations, consistent with previous literature reports.²⁵ To investigate the two distinct dislocation types, we prepared a cross-sectional lamella using focused ion beam (FIB) milling at the specific region indicated by red lines in [Figure S2](#). [Figure 1B](#) presents the corresponding iDPC-STEM image revealing isolated dislocations in the sample. The observed dislocation loops display elliptical morphologies with characteristic dimensions ranging from several nanome-

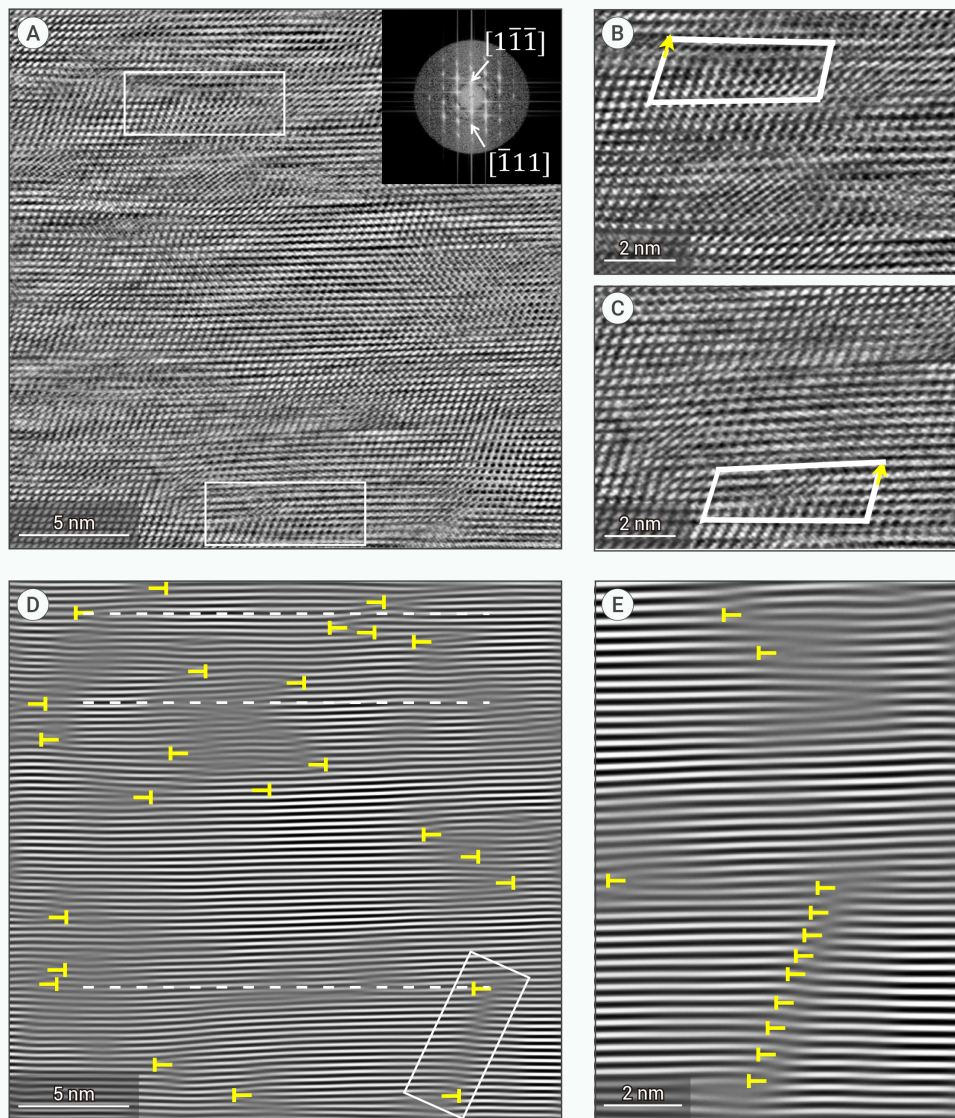


Figure 4. Atomic-scale characterization of GNDs in CaF_2 crystals iDPC-STEM images of GNDs in CaF_2 (A) On-zone atomically resolved iDPC-STEM image of a dislocation obtained using $[110]$ zone axis. (B-C) Enlarged iDPC-STEM image of the local structure in the rectangle in Figure (A). (D) Corresponding inverse FFT image from the $[111]$ and $[\bar{1}\bar{1}\bar{1}]$ spots. (E) Image of stacking fault structure.

lattice to twist and produce microscopic misorientation to form dislocation walls or small-angle grain boundaries. The statistical distribution diagram in Figures 1I-J shows that the maximum misorientation is approximately 1.4° . Specifically, GNDs with an misorientation less than 0.5° account for 99.35%, while those between $0.5^\circ\sim 0.8^\circ$ and $0.8^\circ\sim 1.4^\circ$ account for only 0.56% and 0.09%, respectively. This suggests that GNDs in CaF_2 crystals primarily consist of dense dislocation entanglements, with a small amount of dislocation walls and trace subgrain boundaries.

Atomic structures of SSDs and GNDs

To determine the type of dislocation loops, we firstly studied their Burgers vectors. The TEM dynamic dark-field images are acquired under various $\vec{g}$ conditions, as illustrated in Figure 2. The selected area electron diffraction (SAED) patterns in Figures 2A & E confirm the $[011]$ and $[001]$ zone axis, respectively. Based on this, Figures 2B-D show kinematic bright-field TEM images obtained under various $\vec{g}$ -vector conditions using the $[011]$ zone axis of the same region, while Figures 2F-I show images obtained using the $[001]$ zone axis. At the same position in each figure, the appearance and disappearance of dislocation loops are indicated by solid and dashed circles. Different dislocation loops are denoted by letters A, B and C, as well as red, yellow, and

ters up to 20 nm. Additionally, CaF_2 single crystals were found to remain relatively stable under low-energy electron beam conditions, with no significant morphological or structural alterations. Therefore, low-energy iDPC-STEM are quite suitable to characterize the Burgers vectors of the dislocation loops. A significant and dense cluster of dislocations was observed at the site of regular dislocations, as illustrated in Figure 1C. To analyze the regular dislocations more clearly, geometric phase analysis (GPA) was performed on the aberration-corrected STEM images to assess the dislocation and strain fields associated with the dislocations (Figure 1D).⁶⁰ shown that obvious lattice stress exists in the banded aggregation area with a width of 70 nm, indicating the existence of dislocations in this area. It is worth noting that these dislocations aligned in the same direction as the banded area, which may lead to significant misorientation between the two sides of the area.

To further verify this hypothesis, we quantitatively characterize their misorientation using our self-developed high-resolution EBSD method detailed in the Supplementary Materials (SM). Since HR-EBSD is a micro-region characterization prone to data errors, three random areas shown in an SEM image within the crystal were selected to evaluate the misorientation. The misorientation distribution of dislocations at sites 1, 2, and 3 in Figure 1E are displayed in Figures 1F-H, respectively. It is evident that the misorientation angles of regular dislocations are predominantly within 1° , while the misorientation angles of free dislocations are almost zero. These results indicate that free dislocations don't cause changes in crystallographic orientation, as they store statistical dislocations (SSDs), while regular dislocations are geometrically necessary dislocations (GNDs), which will cause the crystal

lattice to twist and produce microscopic misorientation to form dislocation walls or small-angle grain boundaries. The statistical distribution diagram in Figures 1I-J shows that the maximum misorientation is approximately 1.4° . Specifically, GNDs with an misorientation less than 0.5° account for 99.35%, while those between $0.5^\circ\sim 0.8^\circ$ and $0.8^\circ\sim 1.4^\circ$ account for only 0.56% and 0.09%, respectively. This suggests that GNDs in CaF_2 crystals primarily consist of dense dislocation entanglements, with a small amount of dislocation walls and trace subgrain boundaries.

However, when a higher-energy electron beam was used to enhance the visibility of dislocation loops and confirm their structures, we observed that the dislocations moved rapidly after several seconds of irradiation. This led to the combination and disappearance of dislocations, resulting in the enlargement of defective areas (-). Additionally, under electron beam (200 keV) irradiation, a three-dimensional ordered periodic "cavity" superlattice the CaF_2 single crystal formed, making it challenging to characterize the atomic structures of the dislocations (Figure S3). Figure 3A shows an atomic resolution iDPC-STEM image of the SSDs in the $[110]$ direction. In order to reveal the characteristics of the defects, two regions marked with rectangles in Figure 3A are magnified respectively, as presented in Figures 3B-C. In Figure 3B, fluorine and calcium atoms are observed for the first time in the complete two-dimensional lattice image of the (011) plane of CaF_2 . An extra half atomic plane can be clearly observed in the lattice image surrounding the dislocation core shown in Figure 3C. The Burgers vector was determined as $1/3[111]$,

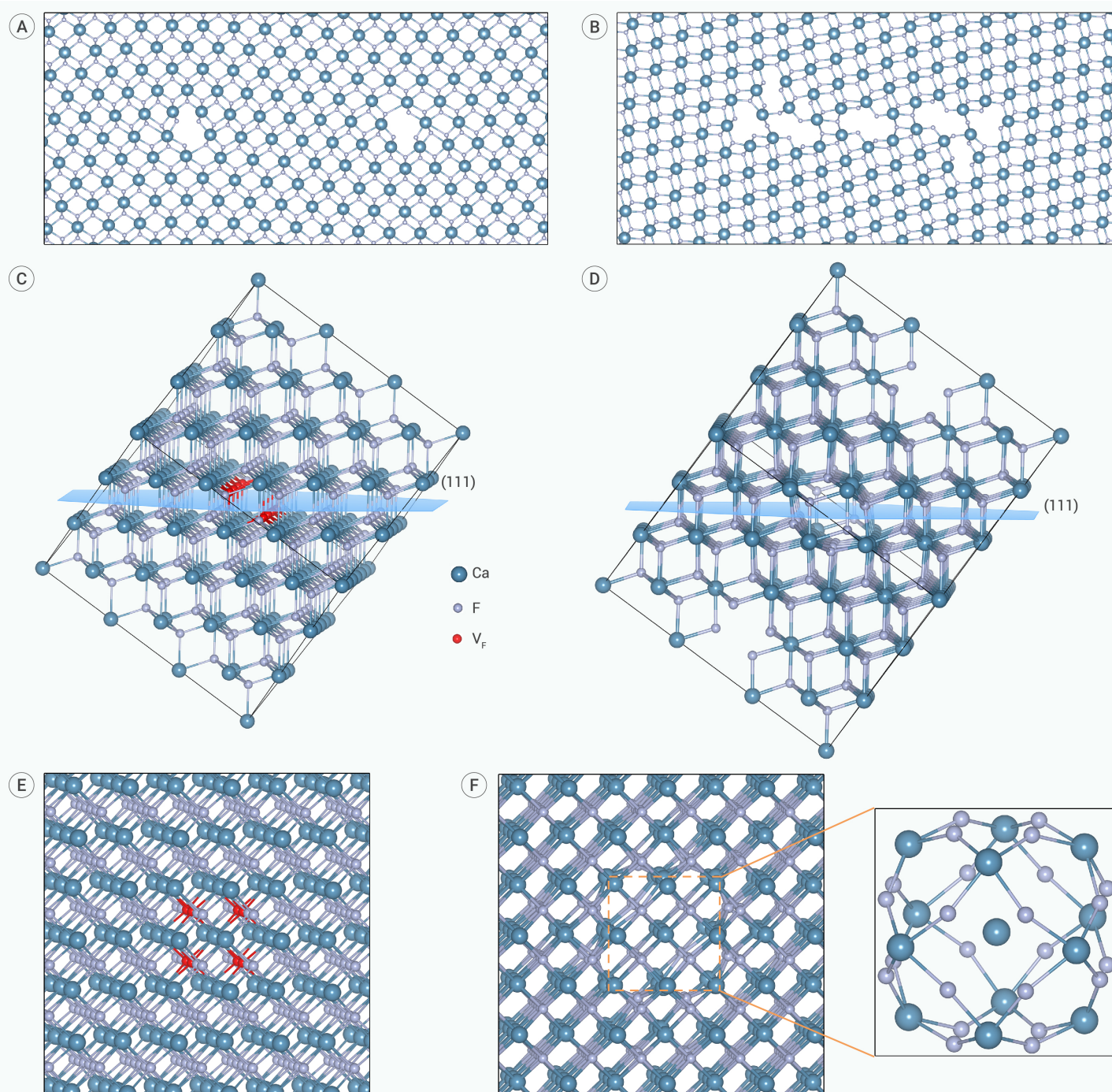


Figure 5. Dislocation Core Structures and Fluorine Vacancy Evolution via Supercell Modeling Atomic structures of (A) a perfect dislocation with a Burgers vector of $1/2[110]$ and (B) a Frank partial dislocation with a Burgers vector of $1/3[111]$. (C) and (D) show clustered F vacancies on the (111) surface before and after relaxation, respectively. (E) and (F) illustrate the formation of a void due to clustered F vacancies before and after relaxation. Two dislocation cores with opposite Burgers vectors are inserted in each supercell to satisfy periodic boundary conditions.

corresponding to a Frank partial dislocation. Moreover, in the vicinity of the dislocation cores, F atoms are severely distorted from its original lattice positions, and absent with only Ca atoms chemically bonded with each other. Figure 3D presents a schematic diagram of the Frank partial dislocation in the atom resolved iDPC-STEM image of Figure 3C, and the Burger vector can be clearly identified. Nevertheless, it is challenging to observe dislocation loops with a Burgers vector $b=1/2[110]$ because they are parallel to the observation direction $[110]$. In order to achieve clearer image of the dislocation loops, the electron beam direction $[122]$ was selected to observe the two-dimensional atomic structure of SSDs, as depicted in Figure 3E. The magnified micrograph in Figure 3F shows the complete two-dimensional planar atomic structure at rectangle position 1 in Figure 3E. A comparison with Figure 3F

reveals an extra half atomic plane around the dislocation core in Figure 3G (magnification of rectangle position 2 in Figure 3E), indicating a Burgers vector of $1/2[110]$, characteristic of a perfect dislocation loop. The schematic diagram of the $1/2[110]$ dislocation loop is shown in Figure 3H. Previous investigations^{12,22,24,46} indicates that the dislocation loops in CaF_2 single crystals are primarily $1/2[110]$ perfect dislocations, while Frank partial dislocations with a Burgers vector of $b=1/3[111]$ have rarely been reported, possibly due to limitations in the characterization techniques.

The two-dimensional atomic structure of geometrically necessary dislocations (GNDs) within the deformation zone was characterized and depicted in Figure 4A. Figures 4B-C correspond to positions 1 and 2 in Figure 4A, respectively, confirming the presence of numerous Frank partial dislocations in

GNDs. The misorientation angles caused by the parallel arrangement of multiple Frank partial dislocations were calculated to be approximately 0.71° , consistent with the HR-EBSD results (Figure S4). Figure 4D shows the inverse FFT image obtained using two (111) points from the inset FFT pattern, specifically $(1\bar{1}\bar{1})$ and $(\bar{1}11)$. The figure reveals that edge dislocations with perpendicular Burgers vectors are aligned in a single direction, forming a “wall-like” morphology. Furthermore, GNDs exhibit local stacking faults, as illustrated in Figure 4E. The boundary between the fracture and non-fracture zones is observed to be a Frank partial dislocation, primarily formed by local insertion or extraction of parts of the {111} plane within the crystal. The inverse FFT image from two (220) points selected from Figure 4A indicates the presence of a small number of randomly distributed perfect dislocations compared to the {111} plane, as shown in the inverse FFT (Figure S5). Thus, GNDs are primarily composed of $1/3[111]$ Frank partial dislocations, $1/2[110]$ perfect dislocations, and local layer dislocations, and $1/3[111]$ Frank partial dislocations being the dominant type. It is important to note that the dislocation arrangement in GNDs differs from that of common small-angle grain boundaries, as the dislocations are not aligned in the same direction, and the dense stacking degree is low (Figure S6).⁶² Therefore, in CaF_2 crystals, GNDs induce lattice distortion and micro-misorientation, rather than small angle grain boundaries.

Formation mechanism of dislocations

Since the dislocation energy is proportional to b^2 (where b is the Burgers vector), smaller Burgers vectors are energetically favorable. Dislocations with higher energy are unstable and tend to decompose into configurations with lower energy through reactions. Therefore, the Burgers vectors b of dislocations are limited to several specific directions with short lattice periodicity. For face-centered cubic (FCC) lattice, the shortest period is $1/2[110]$, with the vector length of $\sqrt{2}/2$, while the Burgers vector of a Frank partial dislocation is $1/3[111]$, with a length of $\sqrt{3}/3$. Although the Burgers vector of a Frank partial dislocation is slightly shorter than that of a perfect dislocation, its core structure is more complex and typically involves the formation of a stacking fault, which may result in a higher formation energy. To investigate this, we calculated the formation energies of perfect dislocations and Frank partial dislocations using first-principles calculations. As shown in Figure 5, the formation energy of Frank partial dislocations ($1/3[111]$) is 6.580 eV/core, which is significantly higher than that of $1/2[110]$ perfect dislocations on {001} planes (2.705 eV/core). This energy difference explains why dislocations in CaF_2 single crystals primarily form with a Burgers vector of $1/2[110]$. CaF_2 single crystals are typically grown using the Vertical Bridgman method. During the growth and cooling stages, an uneven temperature distribution (characterized by a large temperature gradient) within the crystal can induce thermal deformation, leading to residual macroscopic thermal stress, as illustrated in Figure S7. This thermal stress causes lattice misalignment and facilitates the formation of dislocations.^{63–64} Previous studies have also demonstrated that thermal stress is a primary cause of dislocation formation in CaF_2 single crystals.^{16,65} Furthermore, in regions where thermal stress exceeds the critical cleavage stress, the dislocation slip system is activated, resulting in dislocation slip, multiplication, and accumulation.^{63,66} In CaF_2 crystals, the {100}/<110> slip system is activated, and dislocation aggregation is observed (refer to Figure S8). Simultaneously, a significant presence of F vacancies within the crystal structure was revealed employed Energy Dispersive Spectroscopy (EDS) (see Figure S8), which may also contribute substantially to Frank partial dislocations formation. Under high-temperature vacuum conditions, CaF_2 undergoes dissociation, where F^- ions escape and leave behind vacancies.^{63–64} During post-crystallization cooling, these vacancies aggregate and collapse on specific crystallographic planes, inducing contact between adjacent atomic layers and elevating system energy. This process ultimately leads to the formation of dislocations or voids. To quantify the energetics of vacancy-mediated dislocation formation, we performed first-principles calculations. Two distinct vacancy configurations were modeled: (1) eight fluorine vacancies arranged on close-packed {111} planes (Figures 5C–D, unrelaxed vs. relaxed), and (2) vacancies forming a 3D cubic structure (Figures 5E–F). The total energy of the {111}-plane configuration was 8.762 eV lower than the cubic arrangement, yielding a substantial energy gain of 1.095 eV per vacancy. This result highlights a strong preference for vacancies to aggregate on {111} planes, directly facilitating the nucleation of Frank partial dislocations (Figure 5B). To suppress their formation, optimizing crystal growth parameters (e.g., minimizing thermal gradients) and employing a

fluorine-rich atmosphere to reduce F vacancy concentration are critical strategies.

Based on the clarification of dislocation types in the crystal, SSDs are primarily $1/2[110]$ perfect dislocations, while GNDs are mainly $1/3[111]$ Frank partial dislocations. At 400°C , all slip systems in CaF_2 crystals are activated, causing dislocations to move in nearly all directions.⁶⁷ During dislocation migration, when two dislocations with equal and opposite Burgers vectors meet, they may annihilate each other, leading to a reduction in dislocation density. Some perfect dislocations in CaF_2 crystals have opposite Burgers vectors and appear in pairs, making them prone to annihilation (Figure S5). Partial and perfect dislocations merge and rearrange through climbing and slipping, resulting in a reduction in the overall dislocation density. Meanwhile, we characterized the variation in dislocation density at different annealing temperatures and discovered that as the annealing temperature increased from 1000°C to 1120°C , the dislocation density of the crystal significantly decreased, dropping from 10^5 cm^{-2} to 10^3 cm^{-2} (Figure S10). Therefore, by adopting a reasonable heat treatment technique, it is possible to achieve a near-dislocation-free state in CaF_2 single crystals.

CONCLUSION

This study combines optical microscopy, HR-EBSD, and iDPC-STEM to characterize dislocation morphology, misorientation, Burgers vectors, and atomic structures in CaF_2 single crystals. HR-EBSD analysis distinguishes SSDs with negligible misorientation and GNDs with misorientations in three ranges: $<0.5^\circ$ (99.35%), $0.5^\circ\text{--}0.8^\circ$ (0.56%), and $0.8^\circ\text{--}1.4^\circ$ (0.09%). GNDs primarily form dense entanglements, with fewer dislocation walls and subgrain boundaries. SSDs consist mainly of perfect dislocations ($1/2[110]$), while GNDs are dominated by Frank partial dislocations ($1/3[111]$) and stacking faults. iDPC-STEM resolves F/Ca atoms and vacancies, revealing that F-vacancy aggregation and thermal stress drive dislocation formation. These insights guide optimized growth and heat treatment strategies to minimize dislocations in CaF_2 .

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AUTHOR CONTRIBUTIONS

S.L. and Z.B. designed the project. J.D. and Z.Z. developed the growth of CaF_2 single crystal. L.S. performed the sample preparation and structural characterization under the supervision of Z.B. W.Y. performed the characterization of HR-EBSD. Y.K. and L.Z. contributed to the analysis of TEM and iDPC-STEM data. G.S. carried out DFT calculations. L.S. and Z.B. wrote the paper with inputs from W.Y., K.H., Z.Y. and S.L. All authors contributed to the manuscript and approved the final version.

DECLARATION OF INTERESTS

The authors declare no competing interests.

DATA AND CODE AVAILABILITY

All data and code are available from the corresponding authors upon reasonable request.