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In situ TEM study of electron beam stimulated organization of three-dimensional void superlattice in CaF_2

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CaF_2 is widely adopted as a deep-UV window material and thin film optical coating. It has been known that ordered defect superlattices may form in electron irradiated CaF_2.[1] However, the nature of the defects on the superlattice point (i.e., Ca colloids or voids) has not been certain and the self-organization mechanism has not been fully understood. In this study, single crystal CaF_2 were irradiated under 200 keV electron beam at room temperature with in situ TEM observation of the dynamic process of defect ordering. The superlattice reached steady state after an electron fluence of $1\times10^{21}e^-/cm^2$ with the void radius around 5 nm. Videos recorded during the in-situ observation reveal the dynamic self-organization process of the void superlattice. Coalescence was prevalent at the initial stages. Migration and preferential growth were dominant at the final stages of the superlattice formation.

Fig 1 shows the series of TEM images obtained from CaF_2 under 200 keV electrons at the current density of $2\times10^{18}e^-/cm^2s$. The defect superlattice forms at a fluence of $6\times10^{20}e^-/cm^2$. It reached the steady state at $1\times10^{21}e^-/cm^2$ and the superlattice structure was not destroyed until the accumulated electron fluence is higher than $3\times10^{21}e^-/cm^2$. Fig 2 shows 3 sets of through focus images along [100], [110] and [111] directions. Voids which are fully enclosed inside the specimen can be imaged by defocusing the image and observing the special form of phase contrast termed Fresnel contrast. All these features appear black dots in the overfocused images and white dots in the underfocused images. This, with other evidence, suggests these defects are voids in nature. Sample tilting experiments revealed that the void superlattice has a simple cubic structure with the superlattice oriented parallel to the cubic fluorite matrix. It shows square, rectangular and hexagonal patterns along [100], [110] and [111] zone axes of CaF_2 matrix. The edge length of the simple cubic superlattice unit cell lies in the range 15-20 nm, giving the ratio of the superlattice spacing to void radius around 3. Fig 3 is the Ca elemental mapping obtained by Energy Filtered TEM. The darker area in the mapping indicates fewer Ca atoms in the area. In comparison with the BF image, it demonstrates that the Ca atoms were removed from the defect cluster area. This is another solid proof which shows these are real voids, not Ca colloids or anion voids. Thus the fluxes diffusing under the electron irradiation are composed of both Ca and F atoms, actually the stochiometric CaF_2 molecules.

The anisotropic diffusivity of the migrating crowdion may explain the superlattice formation. Interstitials and vacancies are concurrently generated during particle irradiation. Crowdion, consisting of interstitials, migrates along the close-packed directions. Eventually only aligned voids with equal sizes survive throughout the irradiation process. This model explains the isomorphic behavior between void superlattice and host crystal lattice.

Reference:

[1] Johnson, E. and L.T. Chadderton, *Anion Voidage and the Void Superlattice in Electron-Irradiated CaF_2.* Radiation Effects and Defects in Solids, 1983. **79**(1-4): p. 183-233.
[2] This research was supported by US DOE Basic Energy Sciences with grant no. DE-FG02-02ER46005.

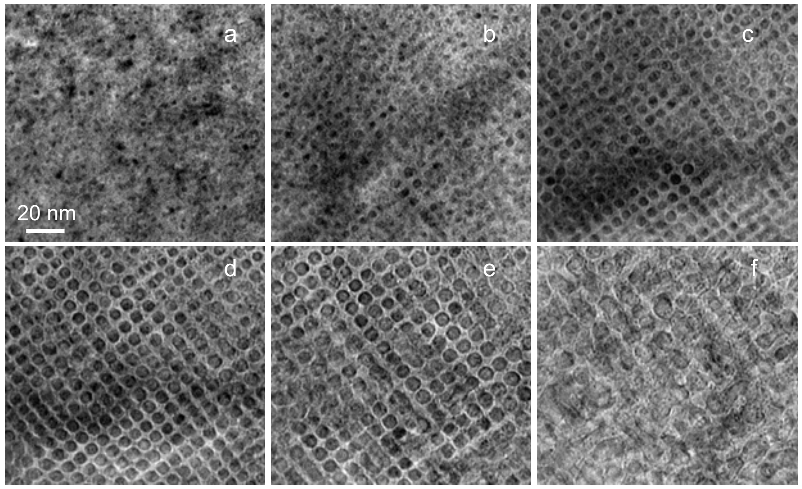

Fig 1. Overfocused bright-field images of voids in CaF_2 recorded during *in situ* TEM with electron fluence of (a) $5\times10^{19}e^-/cm^2$, (b) $4.5\times10^{20}e^-/cm^2$, (c) $1.2\times10^{21}e^-/cm^2$, (d) $2\times10^{21}e^-/cm^2$, (e) $3\times10^{21}e^-/cm^2$, (f) $4\times10^{21}e^-/cm^2$

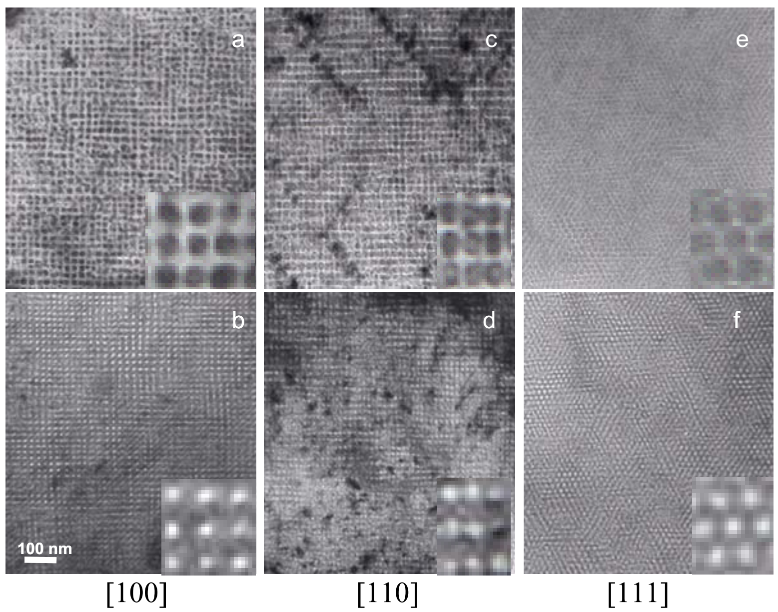

Fig 2. Through focus TEM images along [100], [110] and [111] directions of electron irradiated CaF_2. (a), (c) and (e) are overfocused images and (b), (d) and (f) are underfocused images. Insets are the magnified images showing square, rectangular and hexagonal patterns along three different zone axes.

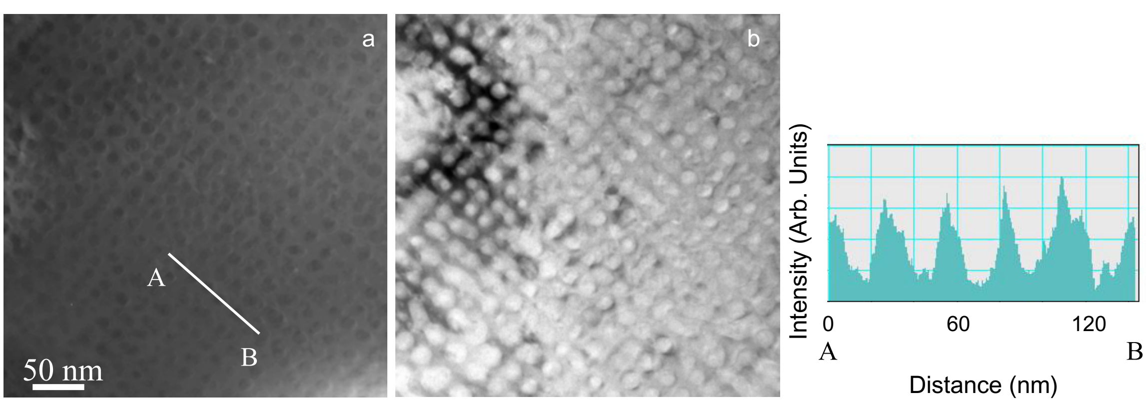

Fig 3. (a) Ca element mapping and (b) bright field image of the same area in electron irradiated CaF_2. The intensity profile along the line indicated in the mapping shows the periodic distribution of the Ca concentration.