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Direct Observation of Defect Dynamics in Nanocrystalline CaF_2 : Results from ^{19}F MAS NMR Spectroscopy

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Sample Synthesis and Characterization

The bulk sample of CaF_2 used in this study was a single crystal that was obtained from the mineral collection of the department of geology at University of California at Davis. Nanocrystalline CaF_2 powder was synthesized via a chemical precipitation method where an aqueous solution of NH_4F was added drop wise to an aqueous solution containing the stoichiometric amounts of $Ca(NO_3)_2 \cdot 4H_2O$. The precipitated CaF_2 was collected by centrifugation and were washed with de-ionized water and acetone followed by drying in a convection oven. Powder x-ray diffraction (XRD) measurements (Scintag XDS-2000) on the nanocrystalline CaF_2 powder indicated that all the peaks appeared in the pattern were consistent with those of a fluorite crystal structure. In agreement with electron probe micro analysis (EPMA) results, no diffraction peaks corresponding to any impurity phase were observed. It may be noted here that the detection limit for XRD is ~ 3 to 5 wt%, significantly higher than that for EPMA (~ 0.1 wt%).

A part of this sample was annealed at 250 °C for 6 hours to obtain ~50 nm diameter nanocrystals. The crystallite size of the nano-crystalline samples was estimated

from the widths of the peaks in the XRD pattern using Williamson-Hall analysis. This estimation was found to be in good agreement with that obtained from high-resolution transmission electron microscope (HRTEM) images of these materials (see Fig. S1 below).

^{19}F MAS NMR Spectroscopy

Ambient temperature ^{19}F MAS NMR spectra were collected at a Larmor frequency of 470.24 MHz (11.7 T) using a Bruker Avance 500 spectrometer and a 2.5 mm Bruker MAS probe. Crushed samples were taken in ZrO_2 rotors and were spun at a rate of 33 kHz. High temperature (100 °C ≤ T ≤ 240 °C) ^{19}F MAS NMR spectra were collected at a Larmor frequency of 188.9 MHz (4.7 T) using a Chemagnetics Infinity spectrometer and a 2.5 mm Chemagnetics double resonance MAS probe. Samples were spun in ZrO_2 rotors at a rate of 23 kHz. Approximately 200 to 400 free induction decays were collected using 90^o rf pulse (1.2 μs) with a recycle delay of 5 s, averaged and Fourier transformed to obtain each ^{19}F MAS NMR spectrum. All ^{19}F MAS NMR spectra were externally referenced to $CFCl_3$. The sample temperature and magic angle spinning were controlled using hot/cold N_2 gas in all experiments. $Pb(NO_3)_2$ was used as an external standard to calibrate the sample temperature against the temperature of the exhaust N_2 gas. Temperature calibration was performed using the well-known temperature dependence of the ^{207}Pb chemical shift of $Pb(NO_3)_2$.[1] The line shapes and spinning sideband patterns of the ^{207}Pb MAS NMR spectra of $Pb(NO_3)_2$ were monitored to ensure correct setting of the magic-angle at various temperatures.

Reference:

1. Takahashi, T.; Kawashima, H.; Sugisawa, H.; Baba, T. ^{207}Pb Chemical Shift Thermometer at High Temperature for Magic Angle Spinning Experiments *Solid State Nucl. Mag. Reson.* **1999**, *15*, 119-123.

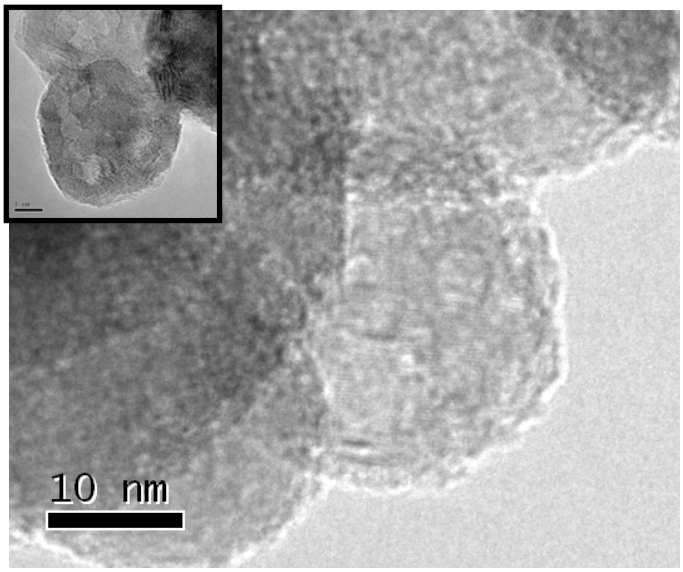

Fig. S1. HRTEM image of nano-crystalline (25 nm diameter) CaF_2. Inset shows a single grain at higher magnification (scale bar = 5 nm).

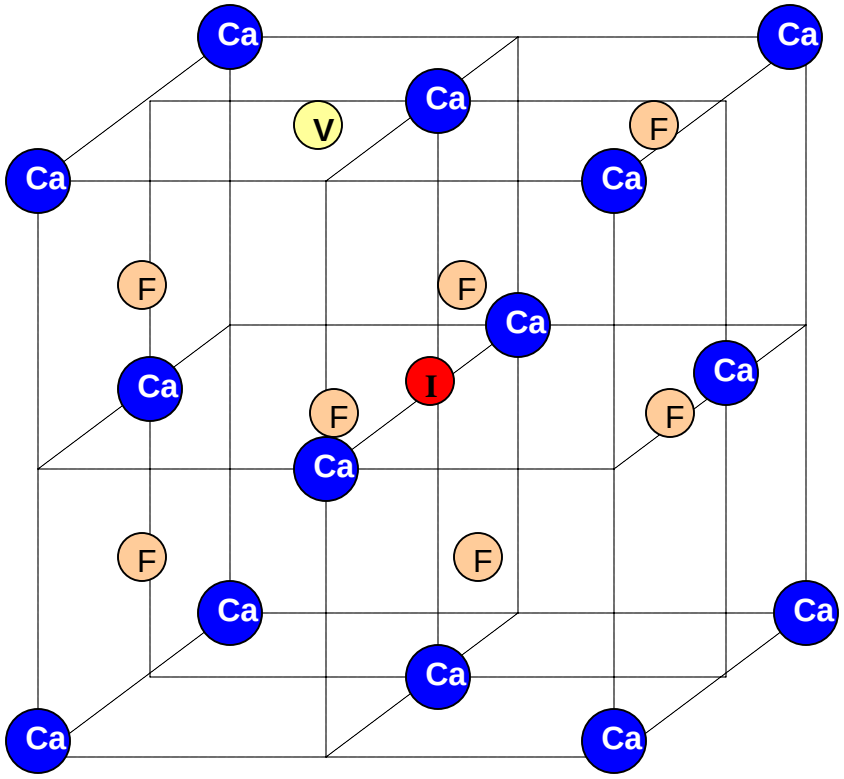

Fig. S2. A vacancy-interstitial pair (Frenkel defect) in CaF_2 lattice. The interstitial fluorine atom denoted by "I" occupies a cubo-octahedral interstitial site in the unit cell. The vacant fluorine lattice site is denoted by "V".

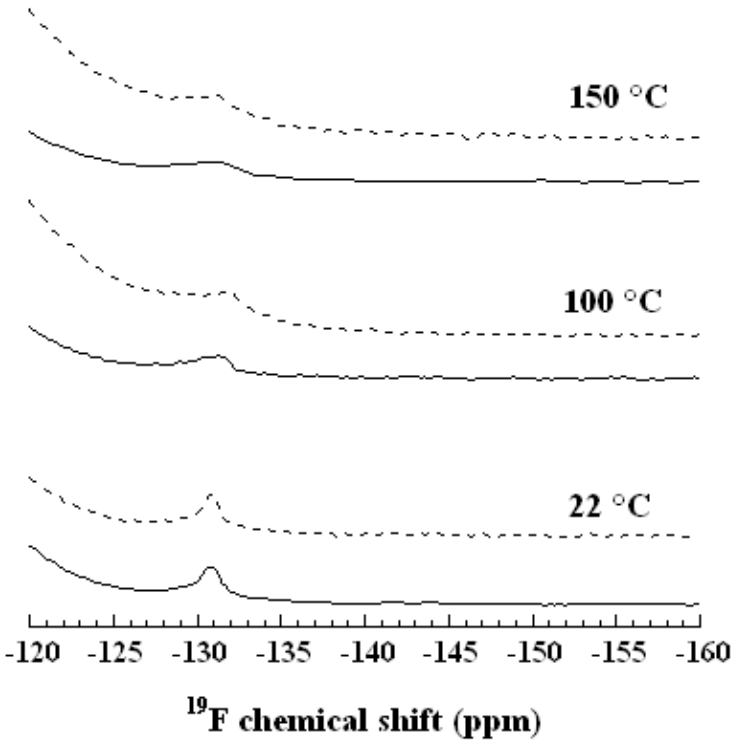

Fig. S3. ^{9}F MAS NMR spectra, in the region between −140 ppm and −120 ppm, of nano-crystalline (~25 nm) CaF_2 collected at identical temperatures during heating (solid line) and cooling (dashed line) showing reversibility of temperature dependent changes in the line shapes.