Influence of Size and Structural Defects on the Vibrational Properties of Lanthanum Hexaboride Nanocrystals

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SUPPORTING INFORMATION

Additional reaction details:

Starting materials were weighed in large batches with an approximate 1to 6.1 ratio of $LaCl_3$ to $NaBH_4$, ground to fine powder using a larger mortar and pestle, well mixed, then stored in an argon glove box until ready for use. Approximately 1g portions of this fine powder mixture was then poured into the ceramic reaction boats when needed and transferred immediately to the reaction oven, where argon was purged for several minutes prior to heating. The reaction time started as soon as the reaction temperature was reached, and it was important that the lid of the tube furnace was lifted immediately upon completing the desired reaction time to allow immediate cooling. Failure to do so gives inconsistent results, as the reaction of the reagents continues until cooled.

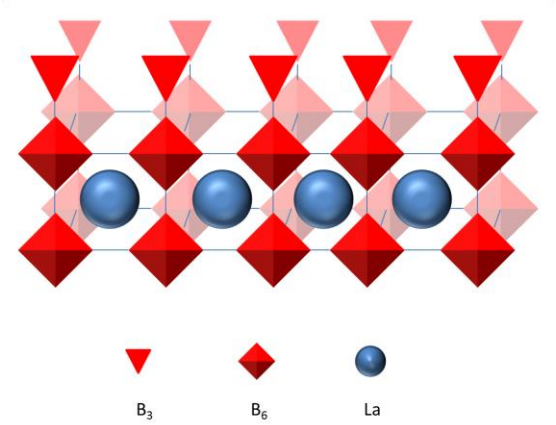

Figure S1. Illustration showing the B_3-terminated surface of LaB_6 nanocrystals

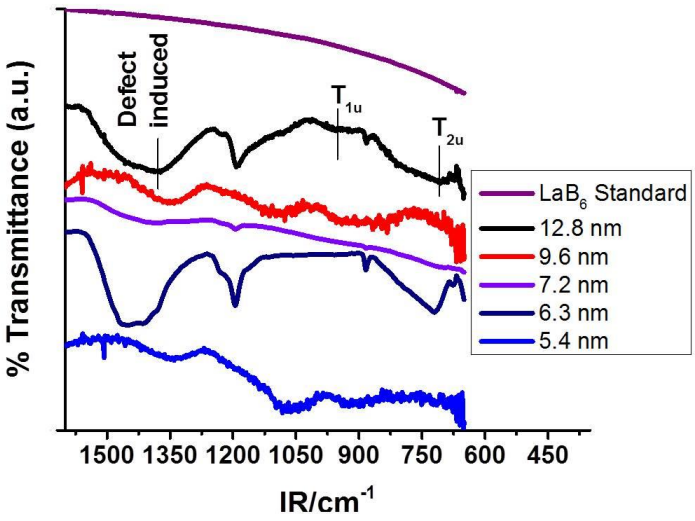

Figure S2. FTIR spectra of LaB_6 nanocrystals demonstrating the large changes of IR-active vibrational states when varying nanocrystal size from 5.4nm to 12.8nm.

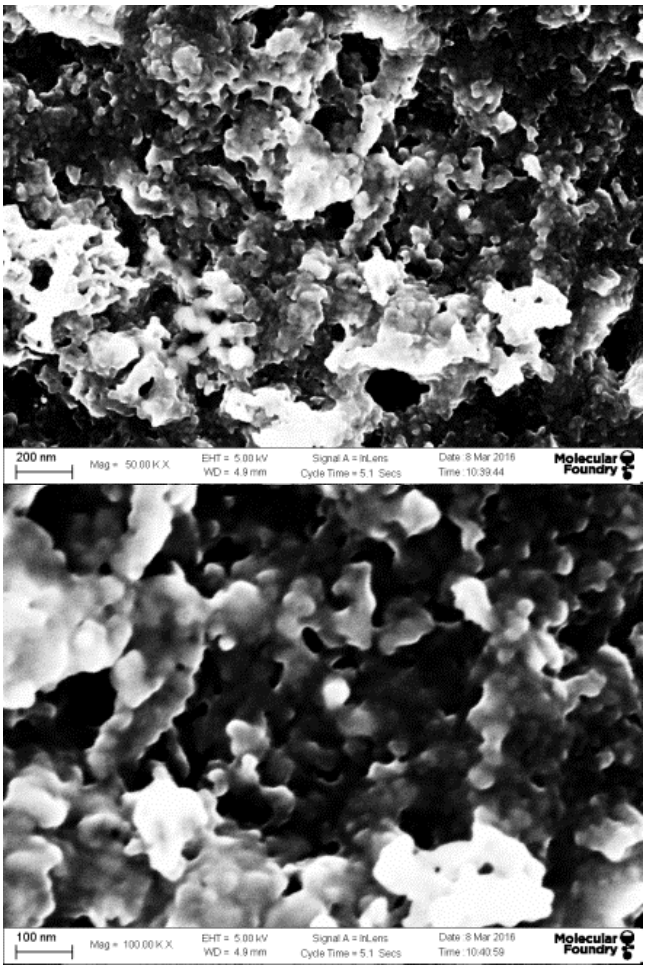

Figure S3. SEM images of LaB_6 synthesized at 400°C for 1 Hr with a heating ramp rate of 60^{o}C/min

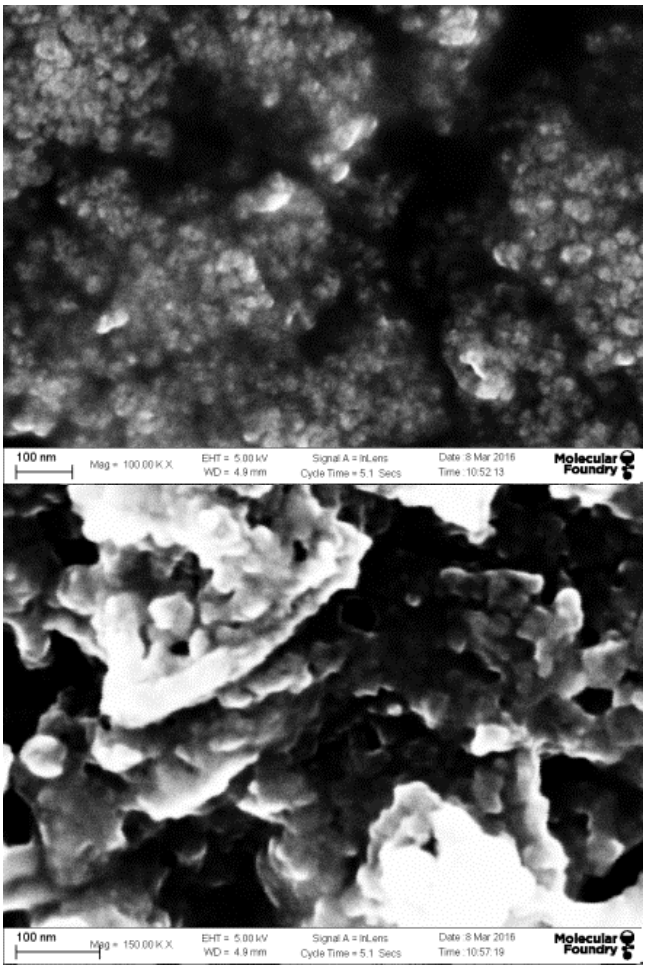

Figure S4. SEM images of LaB_6 synthesized at 450°C for 1 Hr with a heating ramp rate of 60^{o}C/min

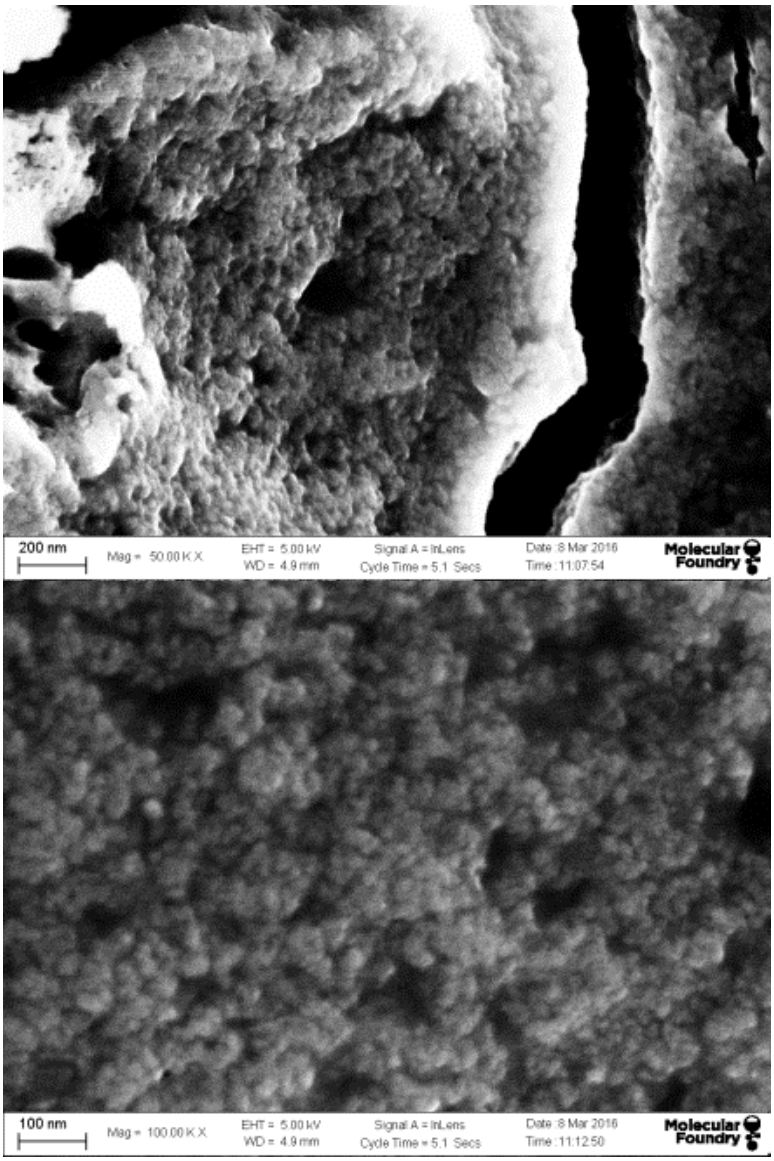

Figure S5. SEM images of LaB_6 synthesized at 500°C for 1 Hr with a heating ramp rate of 60^{o}C/min

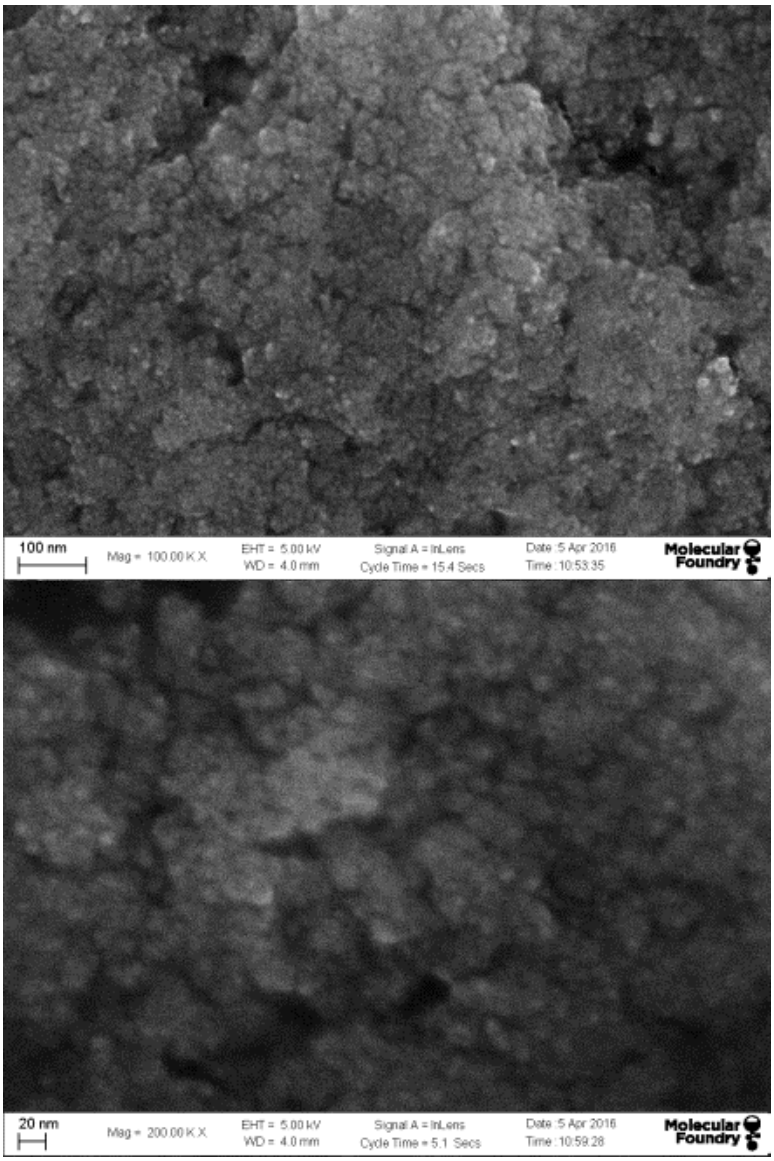

Figure S6. SEM images of LaB_6 synthesized at 550°C for 1 Hr with a heating ramp rate of 60^{o}C/min

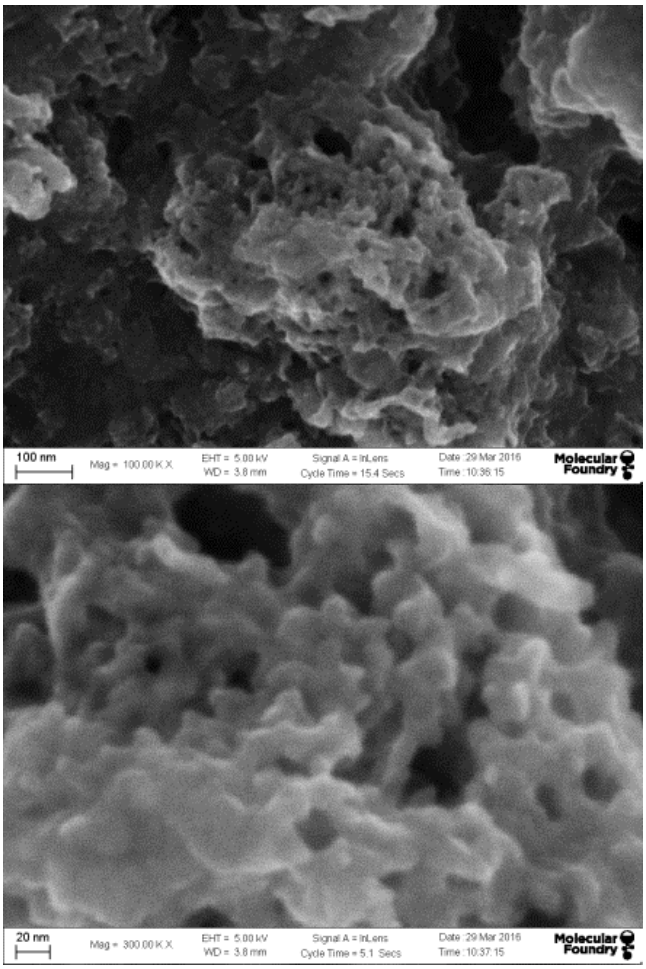

Figure S7. SEM images of LaB_6 synthesized at 600°C for 1 Hr with a heating ramp rate of 60^{o}C/min

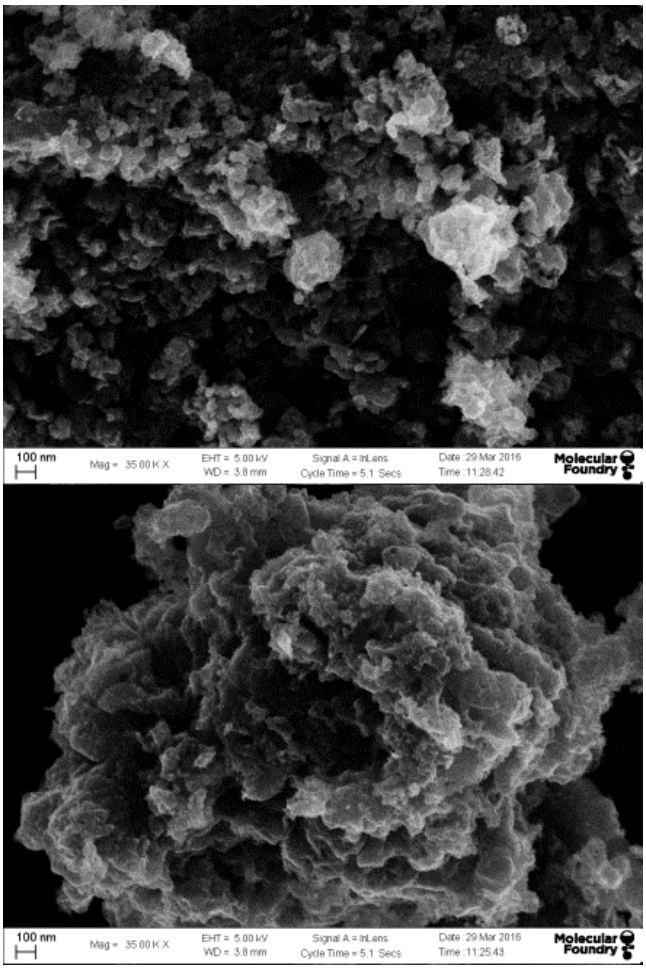

Figure S8. SEM images of LaB_6 synthesized at 700°C for 1 Hr with a heating ramp rate of 60^{o}C/min

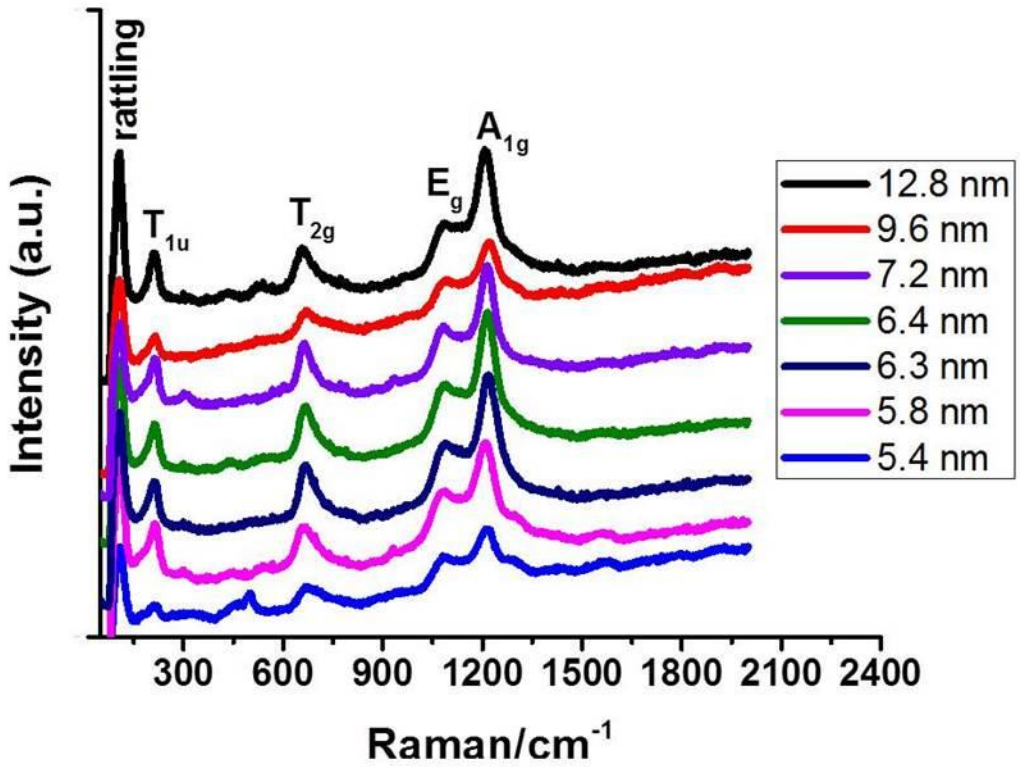

Figure S9. Raman spectra of LaB_6 nanoparticles of sizes ranging from 5.4nm to 12.8nm.

Details of XRD In-Situ Measurement of LaB6 Reaction performed at ALS:

A 1:6 $LaCl_3$ to $NaBH_4$ ratio of powders were mixed and finely ground in a mortar and pestle in an argon atmosphere glove box and placed in 0.7mm diameter quartz capillaries. The capillaries were sealed with wax in the glove box and removed only when the study was performed. Capillaries were mounted on the Huber sample stage on beamline 12.2.2 at the Advanced Light Source (ALS) in Berkeley, CA. Diffraction data were collected on a Mar345 image plate/Perkin Elmer amorphous silicon detector using synchrotron radiation monochromated by silicon(111) to a wavelength of 0.4980Å and a detector distance of 290mm. Distance and wavelength calibrations were performed using a LaB_6 diffraction standard with the program Dioptas [http://www.tandfonline.com/doi/full/10.1080/08957959.2015.1059835], which was also employed for radial integrations. All samples were radiatively heated using IR lamps on a SiC tube with a 2 mm outside diameter by 1 mm inside diameter. This miniature "tube furnace" was equipped with a thermocouple for accurate measurements of the sample temperature and was designed at the ALS [DOI: 10.1063/1.4973561].

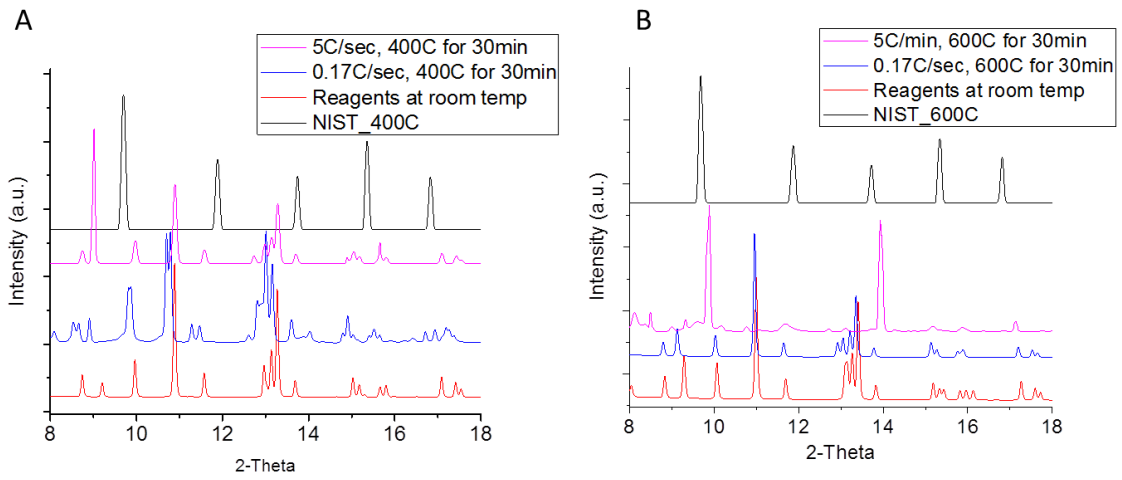

Figure S10. XRD data collected at the Advance Light Source at LBNL comparing a heated NIST LaB_6 standard to reactions of 1:6 $LaCl_3$ to $NaBH_4$ heated at a rate of 0.17°C/sec and 5°C/sec and held for 30min at the final reaction temperature of A) 400°C and B) 600°C.