

Supplementary information:

In the present work, nanocrystalline LaB_6 powder has been synthesized using arc plasma gas phase condensation method. As synthesized powder of LaB_6 contains secondary phases of carbon which form core-shell structure. During emission of electron using field emission microscope, sufficiently high voltage is applied between anode and cathode. In such a case if the aspect ratio of a nano-structure is high, high electric field gets developed across it and hence results into improved emission current. In addition if the electron emission current from core shell structure, electrons are mostly emitted from shell structure. Therefore, to get emission current from core phase i. e. LaB_6 in present case, the as synthesized powder is calcined in air at 923 K for 1h. The structural analysis such as X-ray diffraction pattern and Raman spectroscopy of as synthesized as well as calcined samples has been discussed in manuscript.

The TEM images of as synthesized LaB_6 samples were recorded and presented in the following section. LaB_6 sample synthesized at 100 A (2 kW) and 120 A (2.4 kW) does not show significant amount of carbonaceous species as depicted by XRD and Raman spectroscopic data. The as synthesized samples at 150 A (3 kW) and 170 A (3.4) kW show significant amount of carbonaceous species and therefore investigated using TEM.

LaB_6 powder synthesized at 3 kW (Before calcination):

Bird eye view of the TEM images shown in Fig. 1 (A-B) depicts the LaB_6 powder synthesized by thermal plasma route show presence of carbonaceous species along with LaB_6 particles. The XRD data of the powder synthesized at 3 kW point out towards the presence of carbon along with LaB_6 . On the other hand Raman spectrum does not show any signature of LaB_6 . This observation is similar to that of the LaB_6 powder synthesized at 2.4 kW. This again point out towards core shell structure in which LaB_6 is present at the core and carbonaceous species form shell. In order to give evidence of formation core shell structure, TEM images of the as prepared LaB_6 powder were recorded. TEM images indicate that LaB_6 prepared at 3 kW form of one dimensional structure having diameter 15 - 25 nm, which gives enhanced aspect ratio as compare with the particles. The boundaries of the nanoshaped structure are also seen to be ill defined.

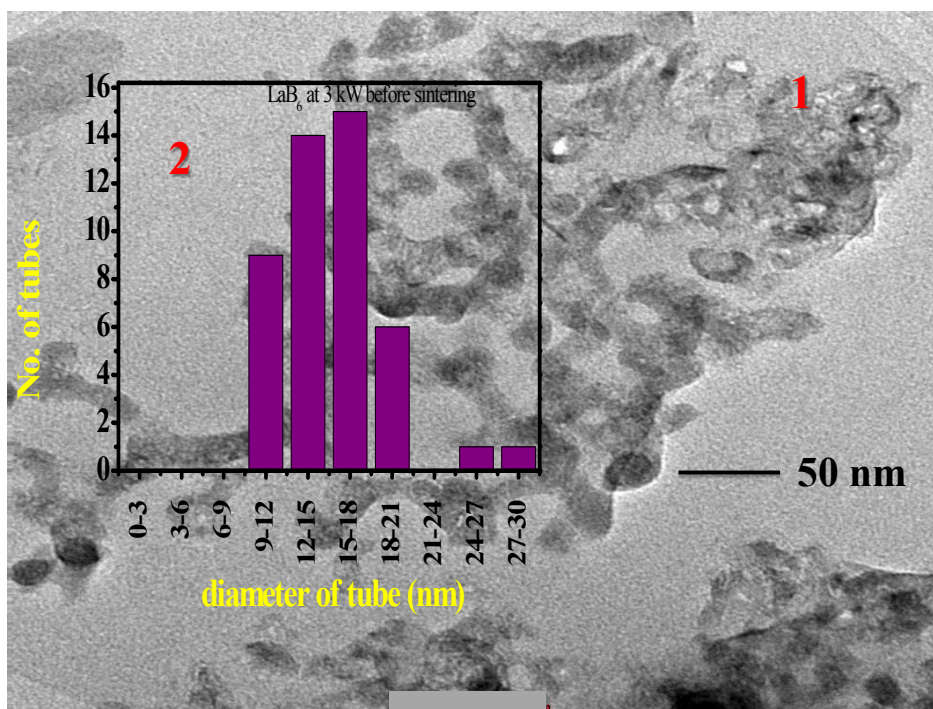


Fig 1(A): TEM bright field image of sample synthesized at 3 kW (1) Bright field image, (2) Particle size distribution

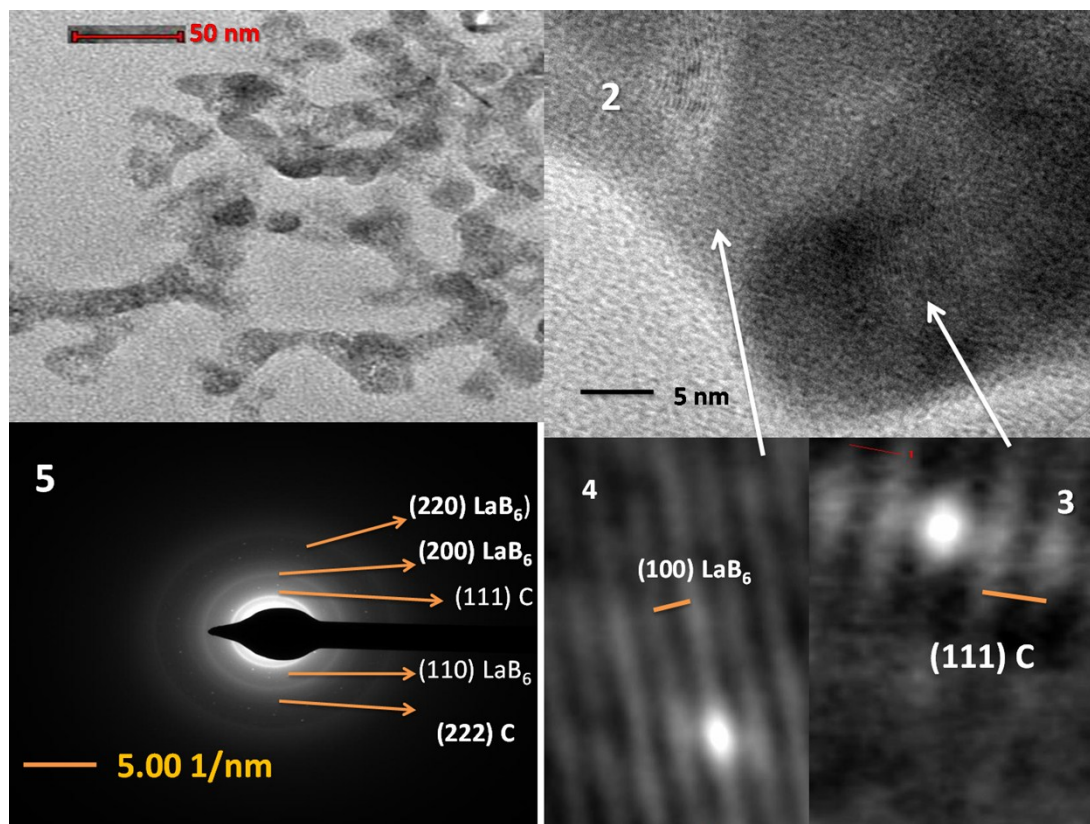


Fig 1(B): TEM images of powder synthesized at 3 kW (before calcination) (1) Bright field image of selected area, (2), (3) and (4) HRTEM pattern (5) SAED pattern

HRTEM image recorded in blackish dark region in the image Fig 1B(2) and (3) indicates presence of carbon on the surface whereas SAED and XRD data indicates presence of both carbon and LaB_6 phase which confirms presence of core-shell made up of LaB_6 – carbon. From HRTEM images shown in the fig. 1B (2,3 and 4) presence of (111) plane of carbon indicates that, carbon is present on the one dimensional structure of LaB_6 . Also in SAED pattern shown in fig. 1 B (5) shows presence of (111) plane of carbon.

LaB_6 powder synthesized at 3.4 kW (Before calcination):

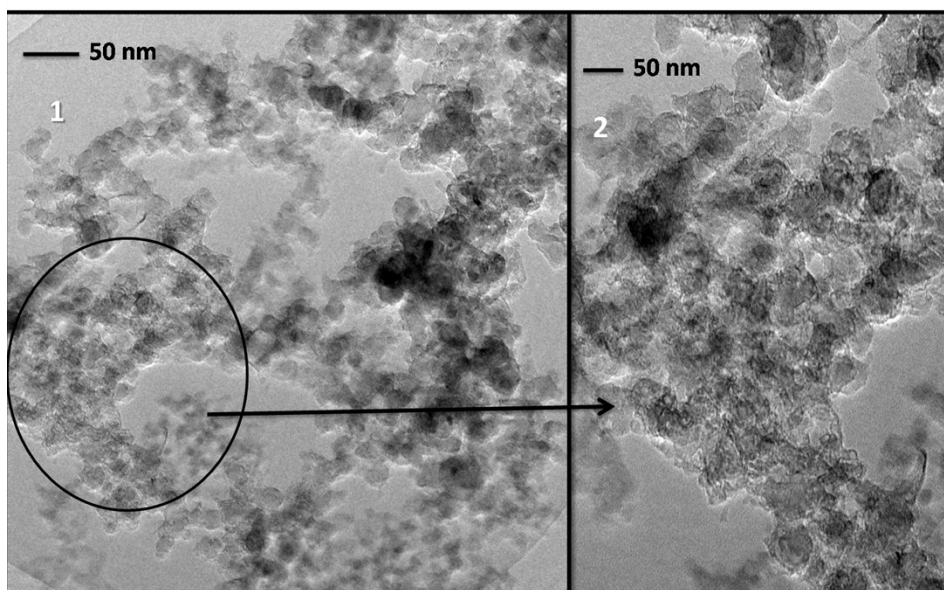


Fig 2(A): TEM bright field image of sample synthesized at 3.4 kW before calcination (1) Bright field image, (2) Magnified part of fig 2A(1)

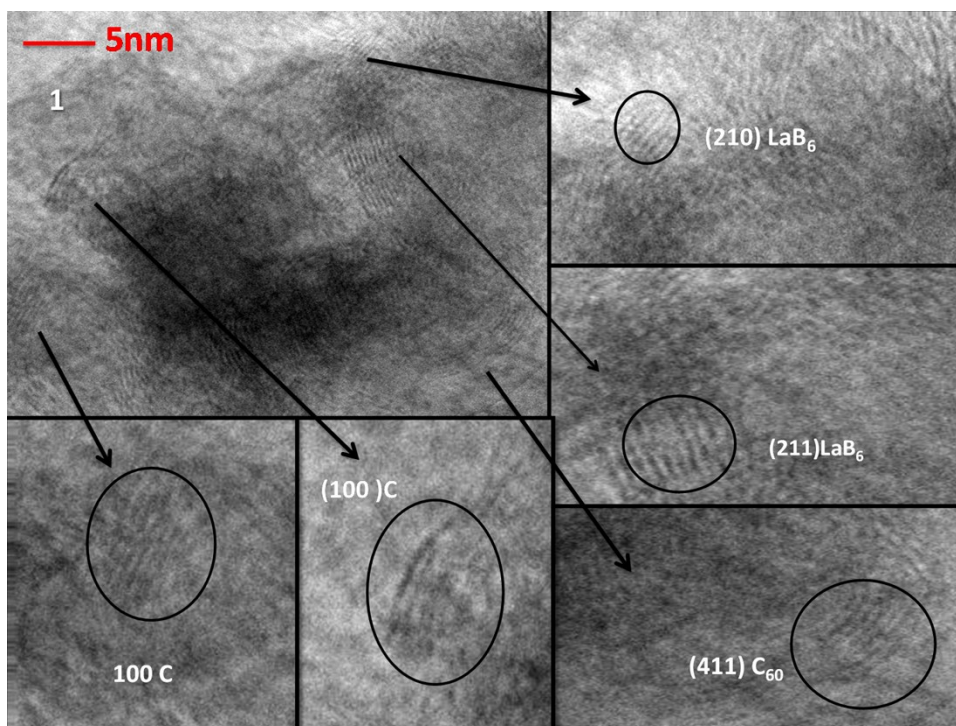


Fig 2(B): TEM images of powder synthesized at 3.4 kW (1) HRTEM pattern

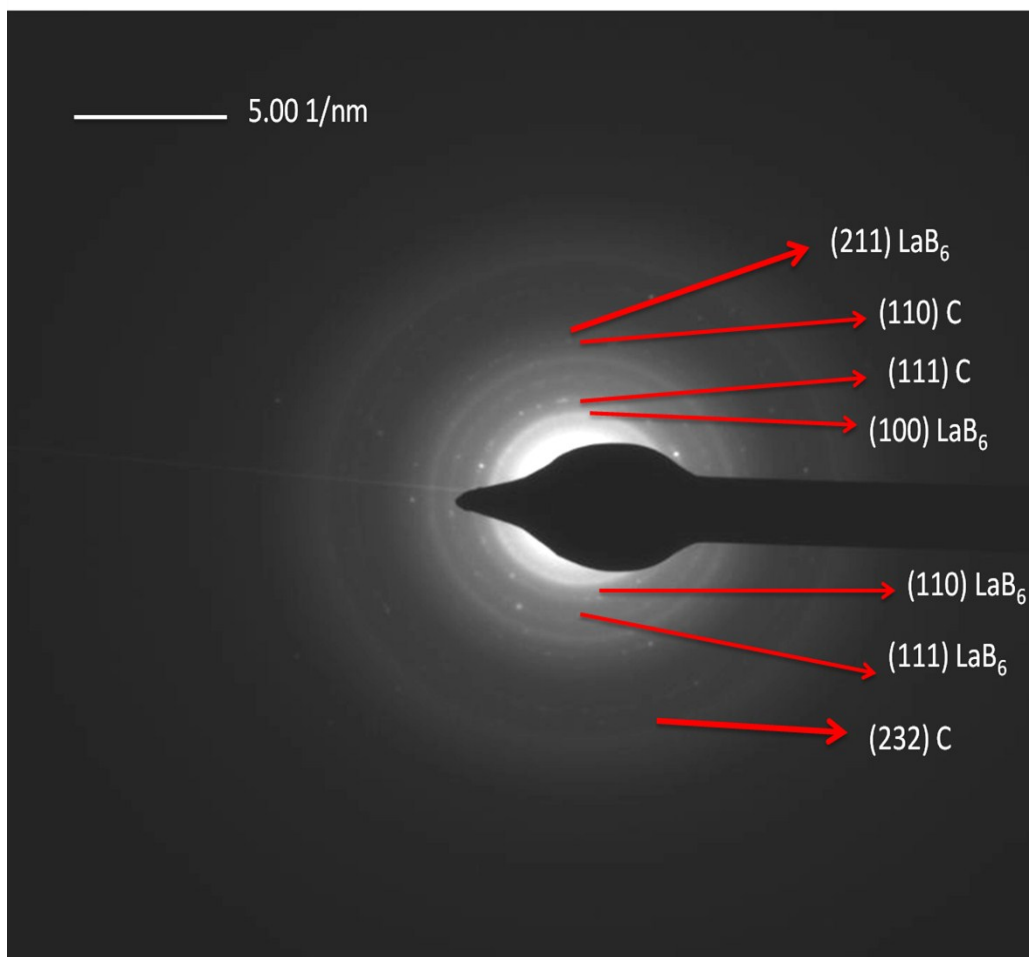


Fig 2 (C): SAED pattern of the LaB_6 synthesized at 170 A (3.4 kW)

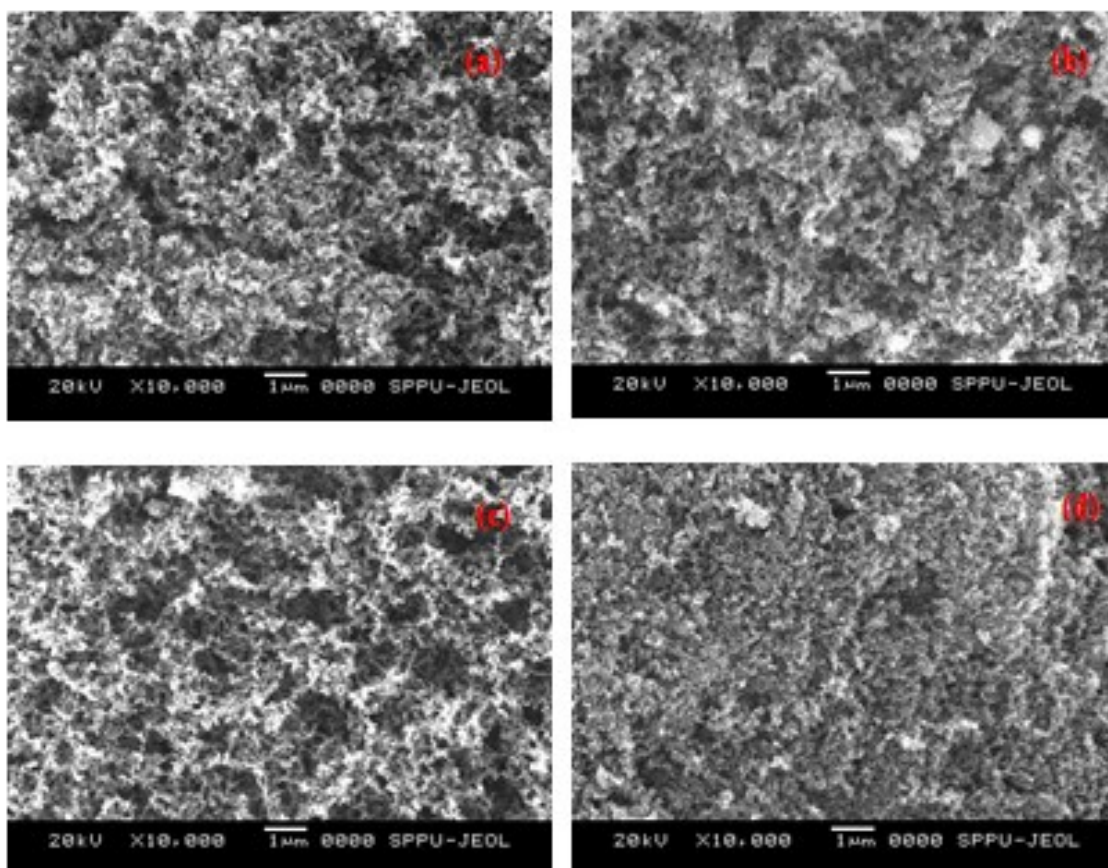
For the LaB_6 powders synthesized at 3.4 kW core shell structure is observed as in other cases as shown in Fig. 2 A (1) and (2). The structure looks like particles are embedded into plane matrix.

From fig 2A (1) and (2) we can see presence of sheet like structures which are agglomerated. HRTEM images recorded in the several regions indicate presence of C_{60}

as a major phase along with LaB_6 which supports inferences based on XRD and Raman spectroscopic data. Diffraction ring observed in SAED pattern also supports presence of C_{60} and LaB_6 nanostructure as a major phase.

From above analysis it is clear as synthesized LaB_6 powder contains carbon as secondary phase and amount of carbon can be minimized by calcination.

Field emission measurement: Field emission current of calcined samples have been recorded to study effect of morphology on emission current density of synthesized LaB_6 samples. For this purpose, powder sample was spread uniformly on carbon tape such that whole area of carbon tape should be covered with LaB_6 powder. Following fig 3 (a-d) shows SEM images of samples spread over carbon tape.



From fig (a-d) it is LaB_6 forms uniform layer on carbon tape which insures that LaB_6 is responsible for the emission current.