Supporting Information

A versatile route for the convenient synthesis of rare earth and alkaline earth hexaborides in mild temperatures

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SI 1. Typical optical images of the as-prepared hexaborides that were recorded by a digital camera with a flash attachment.

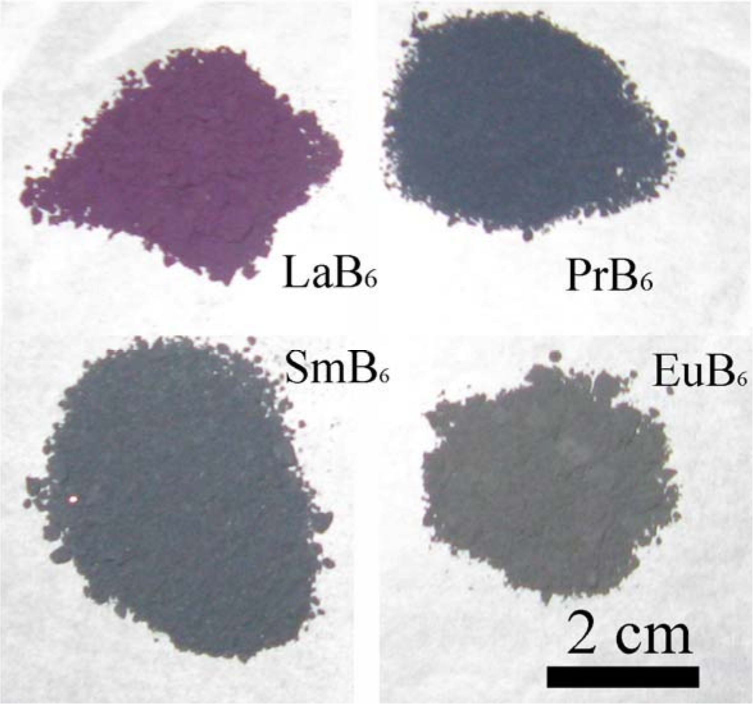

Figure SI 1. Typical optical images of the as-prepared hexaborides.

SI 2 Raman spectra of hexaborides.

The formation of the rare earth hexaborides were also studied by Raman spectra. The *Pm3m* symmetry of the hexaborides structure gives the Raman-active phonons $\Gamma = A_{1g} + E_g + T_{2g}$, which are the vibration of boron octahedra. Fig SI. 2 present the Raman spectra of RB_6 (R =La, Ce, Pr, Nd, Sm, Eu) and AB_6 (A =Ca, Sr, Ba) ranging from 400 to 1800 cm^{-1} obtained at room temperature. Three prominent optical modes can be observed in all of the Raman spectra. The optical mode around ~1250 and ~1100 cm^{-1} can be assigned to the Raman active modes of A_{1g}, and E_g, while the optical modes ranging from 650 to 750 cm^{-1} can be attributed to T_{2g}.[1-3]

The line shape of the E_g mode of divalent EuB_6 and CaB_6, SrB_6, BaB_6 is doublet, while that of E_g mode of the trivalent RB_6 is a broad single peak. Additional peaks around 1400 cm^{-}1 can be observed in trivalent RB_6, the origin of it might caused by electronic state. The peak marked by asterisk in the Raman spectra of S_{Ba} (around 1365 cm^{-1}, near the D-band of carbon) may caused by carbon impurities that originate from the contaminated BaO powder by carbonate in air. The corresponding peak values of those hexaborides match well with the previously reported ones,[1,4-5] indicating the successful synthesis of the hexaborides by an I_2 assistant method in mild temperatures.

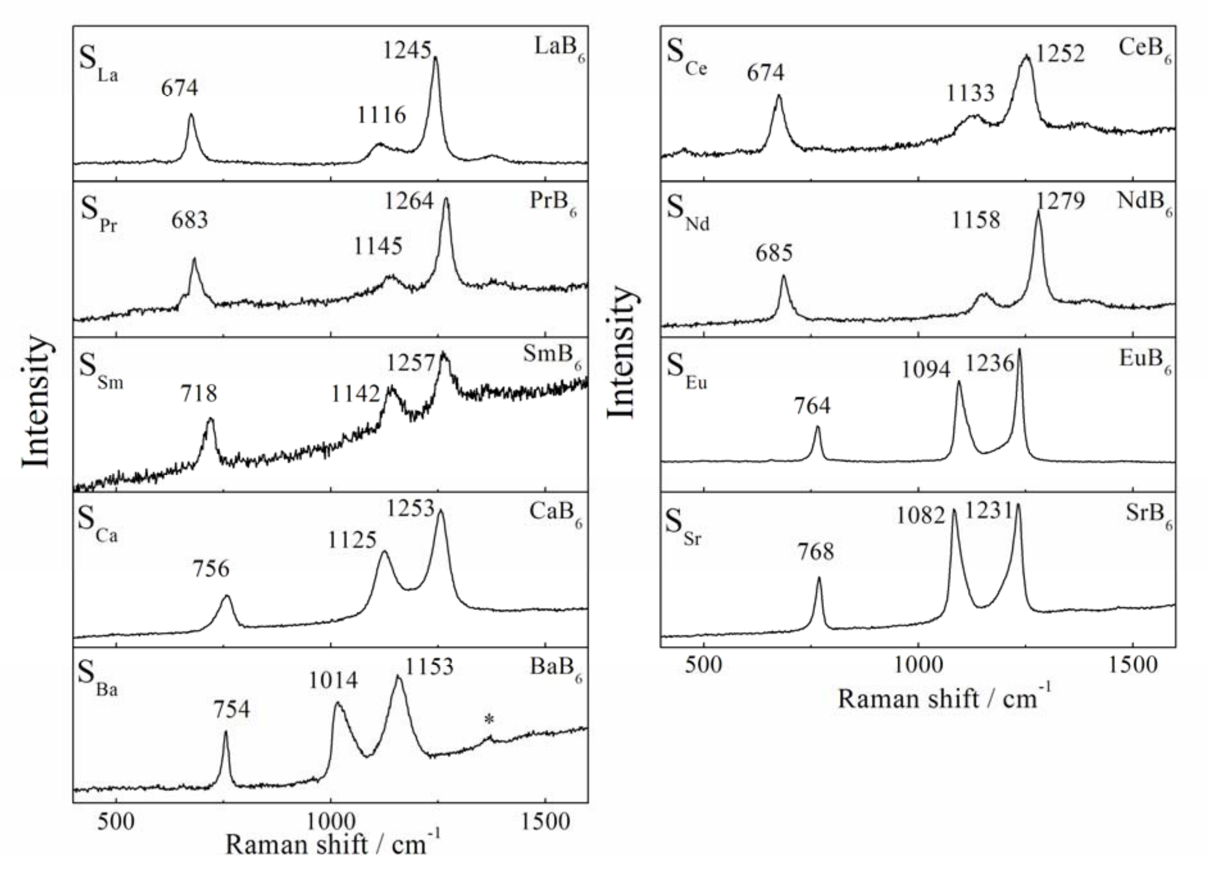

Figure SI 2. Raman spectra of RB_6 and AB_6 (R = La, Ce, Pr, Nd, Sm, Eu; A = Ca, Sr, Ba).

SI 3 TGA analysis of hexaborides

In order to evaluate the thermal stability of the as-prepared hexaborides, the TGA analysis of RB_6 and AB_6 was carried out below 1200 °C in the ambient atmosphere. The TGA curves of those hexaborides shown in Fig. SI 3 indicate that the products have relative high thermal stabilities below 680 °C (except EuB_6, which is below 630 °C). Obvious weight gain starts from 680 °C (630 °C for EuB_6) in TGA curves, which can be attributed to the initial oxidation of hexaborides. The oxidation process below 800 °C produced protective oxides layers on the surfaces of hexaboride grains which protect the hexaborides against further oxidation.[6-7] And a slow weight gain could be observed after the rapid one below 800 °C. As the protective layer could be destroyed due to the B_2O_3 vaporization at higher temperatures, another obvious weight gain is observed in S_{La} and S_{Pr} when the temperature was further increased. Besides, the weight loss near 1200 °C in the S_{La}, S_{Sr} and S_{Ba} may caused by the B_2O_3 vaporization. These results indicate that the thermal stability of the as-prepared hexaborides is stable and basically consist with that of the hexaborides prepared from the boron-thermal reduction process above 1000 °C.[7]

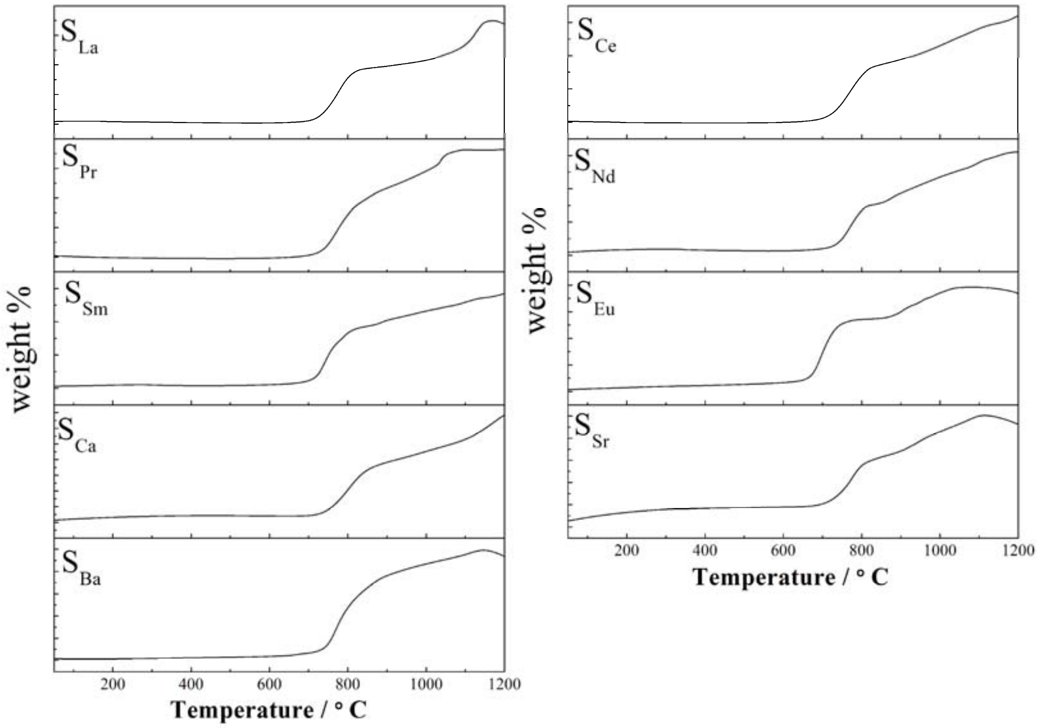

Fig.SI 3. TGA curves of RB_6 and AB_6 (R = La, Ce, Pr, Nd, Sm, Eu; A = Ca, Sr, Ba).

SI 4 XRD patterns of other borides prepared by the I_2-assisted method.

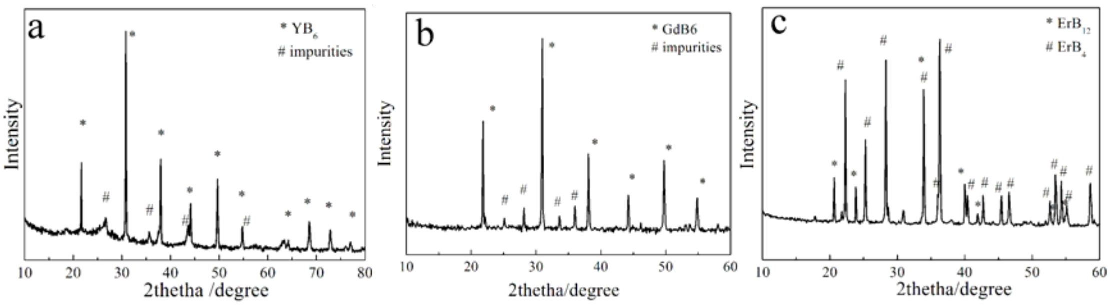

Figure SI 4. XRD patterns of other borides prepared by the I_2 assisted method. YB_6 (a), GdB_6 (b) and borides prepared by Er_2O_3. The samples were prepared by B_2O_3 and corresponding metal oxides at 500°C.

ESI references

1. S. S. Amin, S.-y. Li, J. R. Roth and T. T. Xu, *Chem. Mater.*, 2009, **21**, 763-770.

2. N. Ogita, S. Nagai, N. Okamoto, F. Iga, S. Kunii, J. Akimitsu and M. Udagawa, *Phys B*, 2003, **328**, 131-134.

3. Z. Yahia, S. Turrell, G. Turrell and J. P. Mercurio, *J. Mol. Struct.*, 1990, **224**, 303-312.

4. N. Ogita, S. Nagai, N. Okamoto, F. Iga, S. Kunii, T. Akamtsu, J. Akimitsu and M. Udagawa, *J. Solid State Chem.*, 2004, **177**, 461-465.

5. N. Ogita, S. Nagai, N. Okamoto, M. Udagawa, F. Iga, M. Sera, J. Akimitsu and S. Kunii, *Phys. Rev. B*, 2003, **68**, 224305.

6. S. Q. Zheng, G. H. Min, Z. D. Zou, H. S. Yu, J. D. Han and W. T. Wang, *Rare Met.*, 2002, **21**, 101-105; S. Q. Zheng, G. H. Min, Z. D. Zou and C. Tatsuyama, *Mater. Lett.*, 2004, **58**, 2586-2589.

7. R. K. Islamgaliev, A. V. Zyrin, A. A. Semenov-Kobzar, O. I. Shulishova and I. A. Shcherbak, *Powder Metall. Met. Ceram.*, 1987, **26**, 980-983.