Supplement

Figure S1. Combined Rietveld analysis of NPD (a) and XRD (b) for flux-KBBF powder. Plus (+) marks represent the experimental results and the solid line is from refinement. The ticks indicate the expected positions for structure $R32$. The difference between experimental and calculated results is shown beneath.
Figure S2. Powder SHG intensities of flux-KBBF and hydro-KBBF

Figure S3. The sketch of the geometric relation between bonds and angles in layer (Be$_2$BO$_3$F$_2$)$_\infty$