

X-ray and Neutron Diffraction Studies of Flux and Hydrothermally Grown Nonlinear Optical Material $\text{KBe}_2\text{BO}_3\text{F}_2$

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$\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF) has been known as one of the most important nonlinear optical (NLO) crystals. It is the only NLO crystal which can be used directly in deep ultraviolet (DUV) harmonic generation. Laser radiations of 186.3–200 nm and 156 nm have been generated with KBBF crystals [1,2]. KBBF single crystals can be grown by either flux [3] or hydrothermal [4] methods. Flux-grown (flux-KBBF) crystals have good harmonic generation efficiency with very small crystal size. Though larger crystals can be obtained from hydrothermal method, such crystals (hydro-KBBF) have very low harmonic generation efficiency. In order to understand the reason for the differences between flux and hydrothermal grown crystals, we carried out comparative single crystal X-ray diffractions (XRD) and neutron diffraction (ND) experiments on both hydro- and flux-KBBF single crystals. We also investigate their components with powder XRD and ND, as well as their temperature-dependent behaviours to characterise possible phase transitions.

Single crystal XRD and ND data have confirmed the R32 structure for the flux-KBBF and R-3c structure for the hydro-KBBF samples. While the R32 structure is still valid for the flux-KBBF from powder diffraction data, a mixture of 80.2 wt% of the R-3c structure and 19.8 wt% of the R32 structure was found for the hydro-KBBF. This finding may explain the low harmonic generation efficiency from the hydro-KBBF as the central-symmetric R-3c component should not contribute to the harmonic generation at all.

Temperature dependent XRD did not reveal any phase transition between the R32 and R-3c structures, though the growth temperature for hydro-KBBF is significantly lower than that for flux-KBBF. The current single crystal neutron diffraction did not find evidence of the presence of any hydrogen bond which was originally considered as the force responsible for the formation of large crystals.