Supporting Information

Pressure-induced structural transformations and new polymorphs in $BiVO_4$

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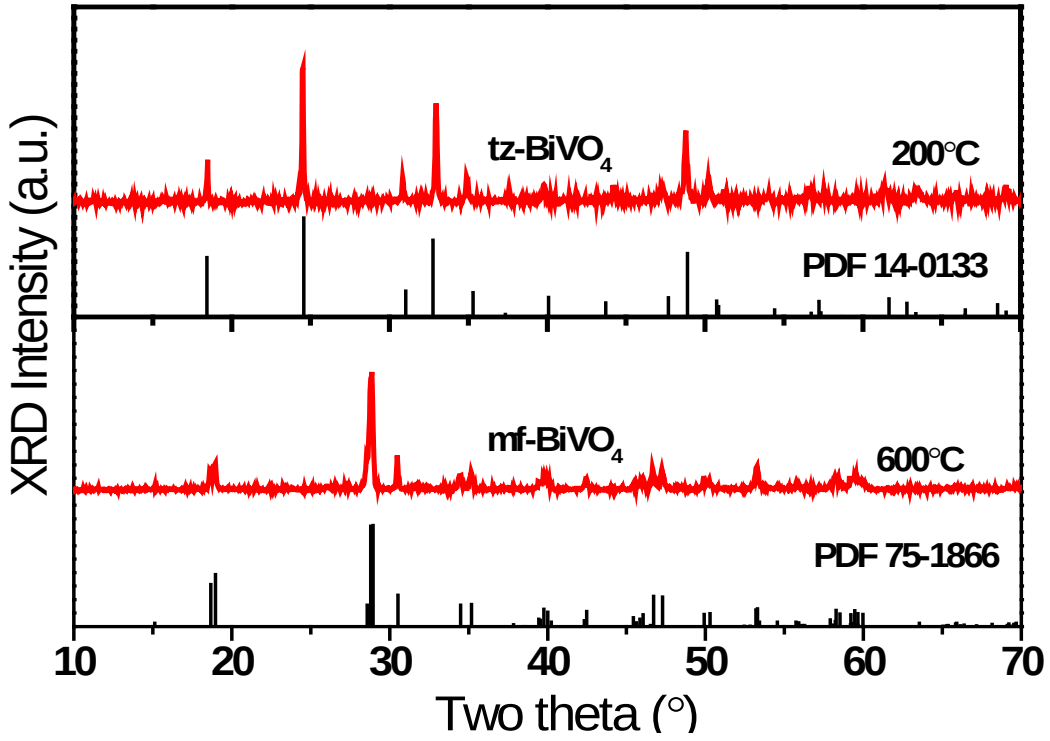

Figure S1. XRD patterns of fergusonite- and zircon-type $BiVO_4$ synthesized using a hydrothermal method.

The crystal structure and phase purity of samples are characterized by XRD analysis, as shown in Figure S1. For the as-prepared sample formed under hydrothermal conditions at 200 °C, its diffraction peaks correspond to those of tetragonal zircon-type $BiVO_4$ (PDF 14-0133). The fergusonite-type $BiVO_4$ transforms to monoclinic fergusonite-$BiVO_4$ (PDF 75-1866) by heat treatment at 600 °C. The observation of no un-indexed reflections and high quality structural refinement results suggest the successful synthesis of high-purity $BiVO_4$ in two distinctive known crystal structures.

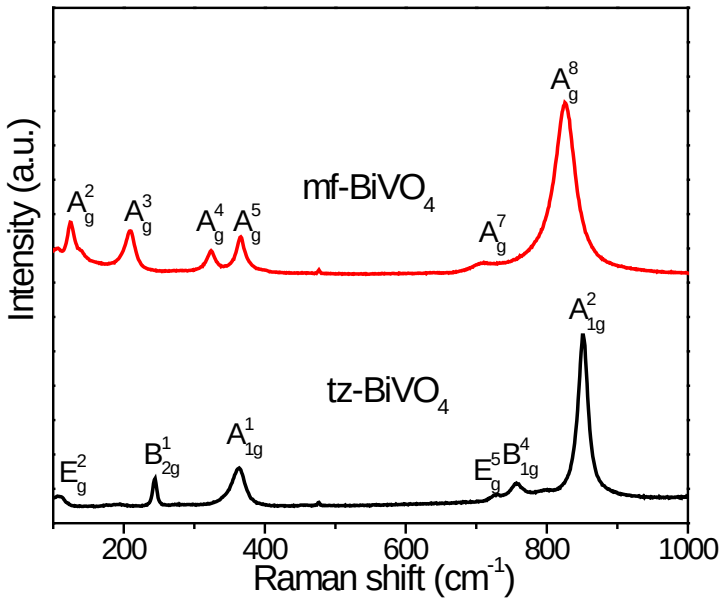

Figure S2. Raman patterns of fergusonite- and zircon-type $BiVO_4$ obtained at ambient conditions.

According to the group theory analysis, there are 18 Raman active modes for mf-$BiVO_4$ represented as: $8A_g+10B_g$ and 12 Raman modes for tz-$BiVO_4$ as $2A_{1g} + 4B_{1g} + B_{2g} + 5E_g$. However, at ambient pressure, only 6 modes and 6 modes are clearly observed for mf-$BiVO_4$ and tz-$BiVO_4$, as shown in Figure S2, because some polarized phonon modes and some weak Raman modes can not be discerned in our experiment. The Raman results have confirmed the successful synthesis of mf- and tz-$BiVO_4$ samples.

Table S1. Observed Raman modes for fergusonite- and zircon-type $BiVO_4$ with assignments.

mf-$BiVO_4$			tz-$BiVO_4$		
Assignment	ω_0	ω_0(Ref18)	Assignment	ω_0(cm^{-1})	ω_0[1]
A^2_g	125	129	E^2_g	109	112
A^3_g	208	213	B^1_{2g}	244	248
A^4_g	324	327	A^1_g	363	367
A^5_g	366	369	E^5_g	728	734
A^7_g	705	708	B^4_{1g}	757	763
A^8_g	825	831	A^2_g	851	857

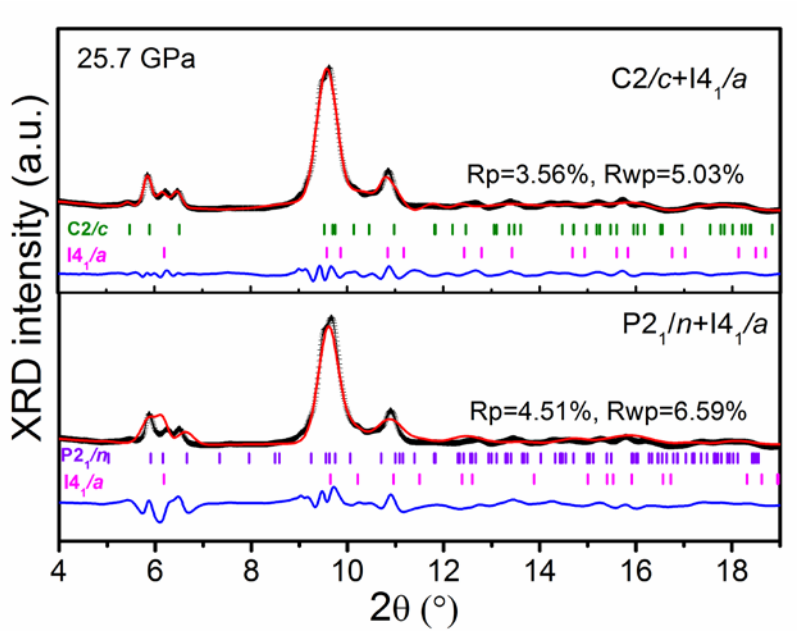

Figure. S3. Comparison of the Reltveld refinement of XRD pattern at 25.7 GPa using *P2₁/n* and *C2/c* structure models respectively. The experimental data are shown as black crosses with refinements shown as red solid lines and the difference between calculated and observed intensities is shown as blue lines. Ticks indicate the positions of Bragg peaks.

To confirm the structure of post-scheelite, we used both $P2_1/n$ and $C2/c$ (β−fergusonite) structural models to refine XRD pattern at 25.7 GPa. As can be seen, the $C2/c$ modes fits the diffraction pattern very well. Moreover, the values of Rp and Rwp further suggest $C2/c$ mode is more sutiable.

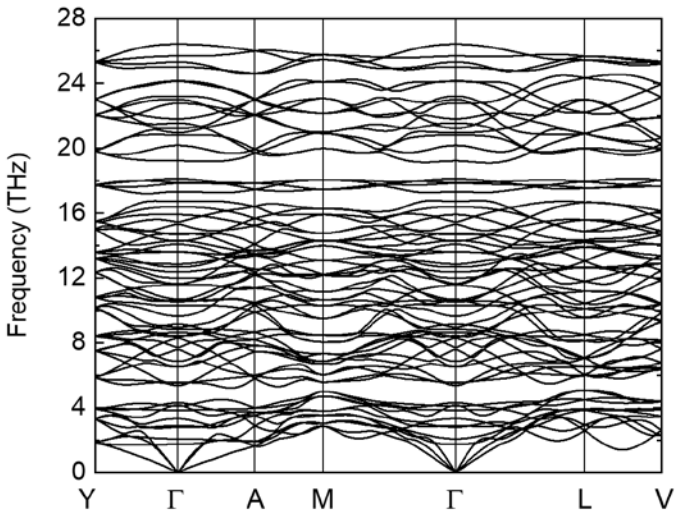

Figure S4. Calculated phonon dispersion relations for β−fergusonite structure at 30 GPa.

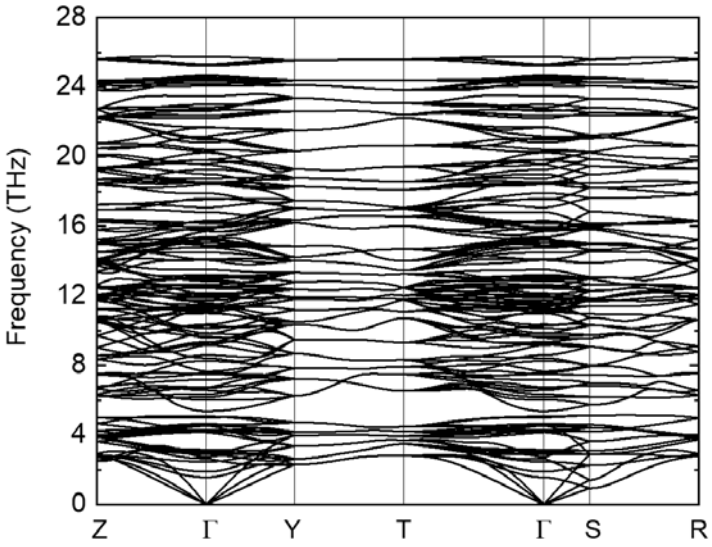

Figure S5. Calculated phonon dispersion relations for the *Cmca* structure at 40 GPa.

Reference

[1] Pellicer-Porres, J.; Vazquez-Socorro, D.; Lopez-Moreno, S.; Munoz, A.; Rodriguez-Hernandez, P.; Martinez-Garcia, D.; Achary, S. N.; Rettie, A. J. E.; Mullins, C. B., Phase Transition Systematics in $BiVO_4$ by Means of High-Pressure-High-Temperature Raman Experiments. *Phys Rev B* **2018**, *98*, 214109.