Supplementary Information

$Bi_{0.33}Zr_2(PO_4)_3$, a negative thermal expansion material with Nasicon-type structure

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Content

Figure S1. TG-DTA traces of $Bi_{0.33}Zr_2(PO_4)_3$

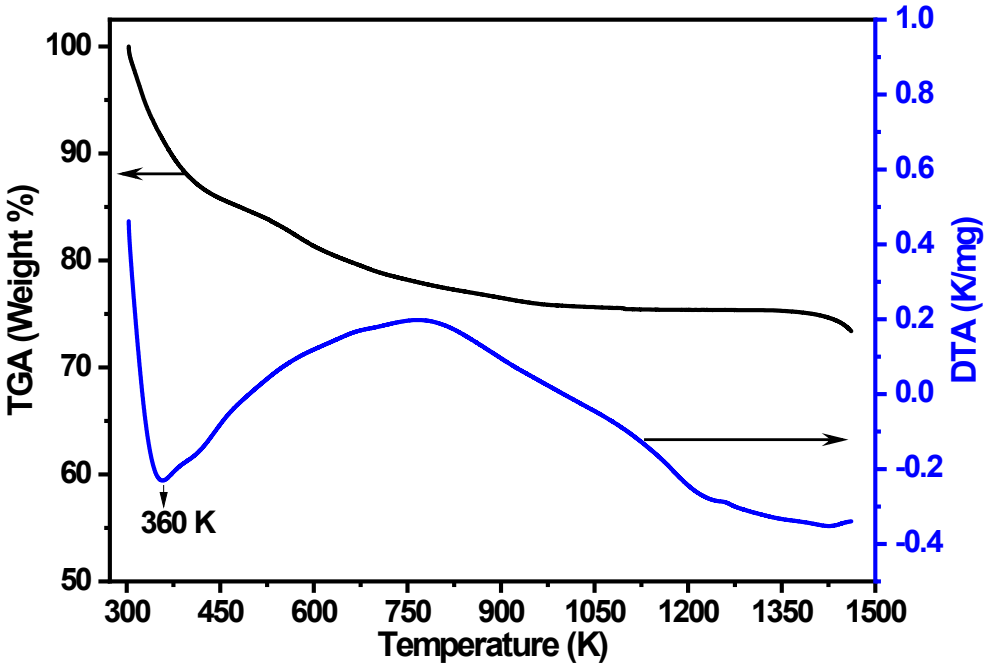

Figure S2. Raman spectrum of $Bi_{0.33}Zr_2(PO_4)_3$

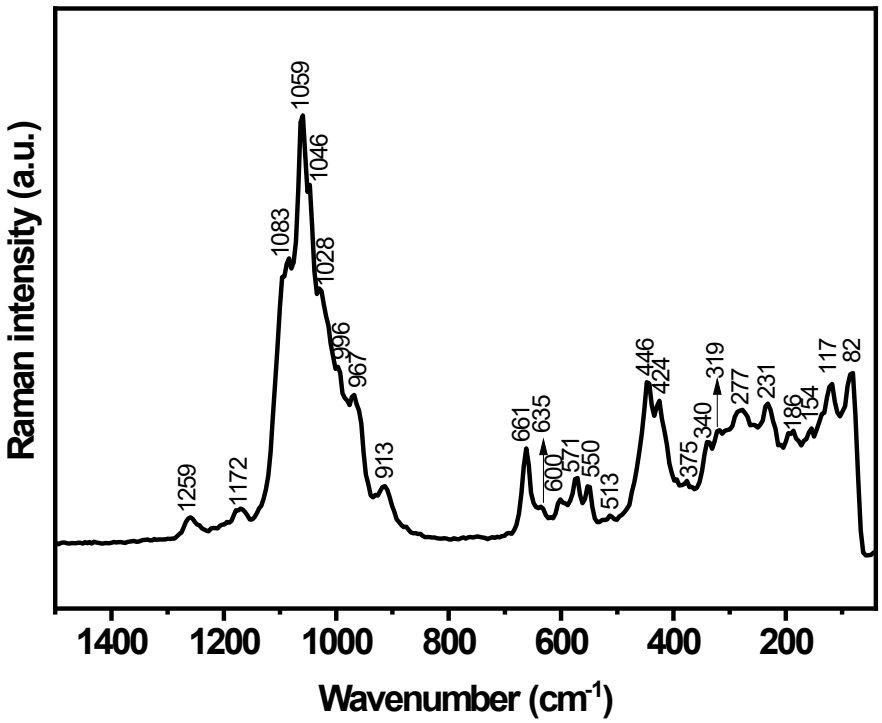

Figure S3. FTIR spectrum of $Bi_{0.33}Zr_2(PO_4)_3$

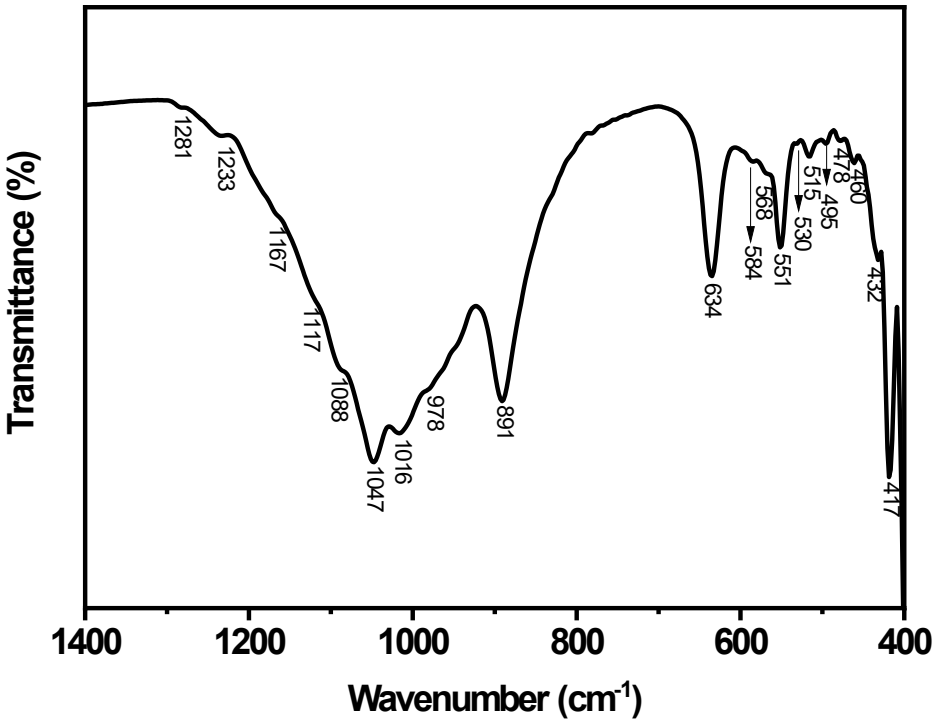

Table S1. IR and Raman peak assignments for $Bi_{0.33}Zr_2(PO_4)_3$

Assignments		$Bi_{0.33}Zr_2(PO_4)_3$	
		Raman (cm^{-1})	***IR (cm^{-1})***
PO_4^{3-}	v_3 (v_{as})	1259 w 1172 w 1083 sh 1059 s 1046 sh 1028 sh 996 sh	1281 w 1233 sh 1167 sh 1117 sh 1088 sh 1047 s 1016 s
	v_1 (v_s)	967 sh 913 sh	978 sh 891 s
	v_4 (δ_{as})	661 s 635 sh 600 sh 571 w 550 w 513 w	 634 s 584 w 568 w 551 s 530 w 515 w 495 w 478 w 460 w
	v_2 (δ_s)	446 s 424 sh	432 sh 417 s

Table S2. Variation of 2θ values with temperature for $Bi_{0.33}Zr_2(PO_4)_3$

Bonds	300 K	373 K	473 K	573 K	673 K	773 K	873 K	973 K	1073 K
Bi1 – O4 (x 6)	2.69081	2.5078	2.76305	2.665	2.66526	2.65082	2.67025	2.72429	2.66731
Zr1 – O4 (x 3)	1.81198	1.98455	1.872	1.77092	1.75789	1.91055	1.67803	1.75927	1.68313
Zr1 – O1 (x 3)	2.17175	2.08658	2.0091	2.18483	2.17625	1.97782	2.26419	2.09673	2.25705
Zr2 – O2 (x 3)	1.91605	1.82217	2.17229	1.88861	1.92775	1.98095	1.90554	1.99542	1.90359
Zr2 – O5 (x 3)	2.17728	2.12716	2.21586	2.18285	2.17528	2.19862	2.16467	2.52786	2.16412
Zr3 – O3 (x 3)	1.99923	1.89977	2.02456	2.00672	2.00433	2.16096	1.9252	2.03031	1.94819
Zr3 – O6 (x 3)	2.23741	2.12815	2.47519	2.20204	2.22038	2.25663	2.30242	2.2509	2.26941
P1 – O1 (x 2)	1.25235	1.69908	1.24984	1.44421	1.36882	1.51822	1.22664	1.56828	1.19846
P1 – O6 (x 2)	1.61108	1.79372	1.94618	1.40939	1.49936	1.55843	1.62759	1.63853	1.66938

hkl	300 K	373 K	473 K	573 K	673 K	773 K	873 K	973 K	1073 K
100	11.56685	11.59017	11.59857	11.60212	11.61985	11.64155	11.66355	11.68156	11.68895
102	13.85593	13.87117	13.92889	13.93804	13.94584	13.94587	13.96779	13.97774	13.98204
104	19.19368	19.21353	19.36578	19.36832	19.36273	19.35346	19.35999	19.36519	19.38288
2-10	20.13308	20.15468	20.15378	20.16860	20.20055	20.22812	20.24430	20.25419	20.26214
200	23.21336	23.23569	23.30529	23.31552	23.33073	23.34551	23.35472	23.36928	23.37985
204	27.96888	27.99481	28.09261	28.10476	28.11668	28.12921	28.13827	28.15166	28.16604
2-16	30.74819	30.77808	30.99144	30.98734	30.96695	30.94661	30.95407	30.96996	30.98917
108	33.01731	33.02613	33.34395	33.33346	33.29925	33.26034	33.26267	33.28469	33.30517

P2 – O5	1.49945	1.37992	1.56287	1.48145	1.59195	1.48799	1.49335	1.20073	1.38577
P2 – O2	1.77243	1.89171	1.66293	1.72077	1.65782	1.53172	1.75953	1.39358	1.74938
P2 – O3	1.53715	1.86328	1.56287	1.57067	1.61724	1.67509	1.52643	1.41258	1.54259
P2 – O4	1.78777	1.59189	1.56675	1.82897	1.68219	1.70204	1.78048	2.12166	1.74938

Table S3. Bond length changes of $Bi_{0.33}Zr_2(PO_4)_3$ as a function of temperature