Polysomatic Apatites - Supplementary Data Section

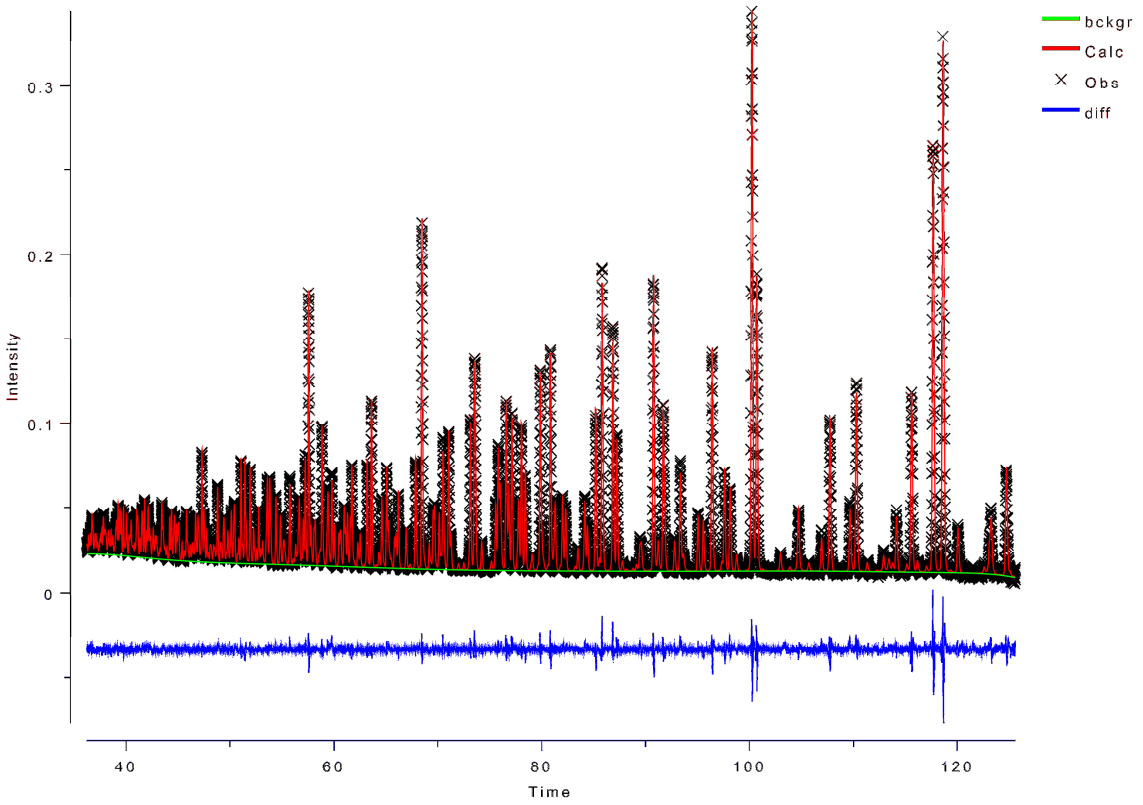

Figure S1a. TOF neutron diffraction profile for $Pb_{15}(Ge_2O_7)_3(GeO_4)_3$ in *P*3.

Table S1a. Refined crystal data for ganomalite, $Pb_{15}(Ge_2O_7)_3(GeO_4)_3$ in *P*3

S.G.	*P*3	a = 10.22887(1) Å	c = 10.66337(2) Å	wRp = 0.043 R_F = 0.036
Site	***x***	***y***	***z***	**100 × U_{Iso}**
Pb(1)^F	1/3	2/3	0.3346(11)	1.9(2)
Pb(2)^F	1/3	2/3	0.6581(11)	0.6(1)
Pb(3)^F	2/3	1/3	0.3241(9)	1.4(1)
Pb(4)^F	2/3	1/3	0.6715(11)	2.0(1)
Pb(5)^F	1/3	2/3	0.997*	0.6(1)
Pb(6)^F	2/3	1/3	-0.0048(12)	1.5(1)
Pb(7)^T	0.2700(3)	0.2714(3)	0.1771(9)	1.71(6)
Pb(8)^T	0.2569(3)	0.2532(3)	0.8110(9)	0.99(6)

Pb(9)^T	0.2512(3)	0.9939(4)	0.5111(9)	1.35(6)
Ge(1)	0.0195(3)	0.3960(3)	0.1422(9)	0.94(1)
Ge(2)	0.0042(5)	0.3859(4)	0.8380(9)	1.15(9)
Ge(3)	0.3944(4)	0.3869(3)	0.4970(9)	0.94(5)
O(1)	0.0959(5)	0.3218(6)	0.2556(10)	2.1(1)
O(2)	0.0880(6)	0.3297(6)	0.7300(10)	1.5(1)
O(3)	0.1229(5)	0.5963(6)	0.1531(11)	2.3(1)
O(4)	0.0842(5)	0.5850(6)	0.8358(10)	1.4(1)
O(5)	0.8290(5)	0.3272(5)	0.1625(10)	2.1(1)
O(6)	0.8096(6)	0.2890(6)	0.8332(9)	1.4(1)
O(7)	0.0666(4)	0.3551(4)	0.9886(11)	1.34(9)
O(8)	0.2950(4)	0.4840(5)	0.4991(11)	1.3(1)
O(9)	0.5859(6)	0.5036(6)	0.5317(9)	2.1(1)
O(10)	0.3729(6)	0.2879(6)	0.3613(10)	2.0(1)
O(11)	0.3185(6)	0.2420(6)	0.6146(10)	2.1(1)

Table S1b. Selected bond distances and angles for $Pb_{15}(Ge_2O_7)_3(GeO_4)_3$

Ge-O tetrahedra			
Germanium (1)	Distance or Angle	Pb(8)^T	
O(1)	1.781(6)	O(2)	2.387(6)
O(3)	1.778(6)	O(4)	2.225(6)
O(5)	1.722(6)	O(6)	2.666(6)
O(4)	1.814(7)	O(11)	2.207(5)
O(1)-Ge(1)-O(3)	108.2(3)	O(2)-Pb(8)-O(4)	84.7(2)
O(1)-Ge(1)-O(5)	111.9(3)	O(2)-Pb(8)-O(11)	86.9(2)
O(1)-Ge(1)-O(7)	107.3(3)	O(4)-Pb(8)-O(11)	96.1(2)
O(3)-Ge(1)-O(5)	111.3(3)		
O(3)-Ge(1)-O(7)	104.5(3)	Pb(1)^F (Triangular pyramid to	
O(5)-Ge(1)-O(7)	113.3(3)	3 equivalent O8 atoms)	
Germanium (2)			
O(2)	1.698(7)	O(8)	2.447(9)
O(4)	1.775(7)	O(3)	2.771(8)
O(6)	1.724(7)		
O(7)	1.814(7)	Pb(2)^F	
O(2)-Ge(2)-O(4)	111.0(3)	O(8)	2.406(8)
O(2)-Ge(2)-O(6)	114.7(3)	O(4)	2.941(7)
O(2)-Ge(2)-O(7)	105.1(3)		
O(4)-Ge(2)-O(6)	113.4(3)	Pb(3)^F (Triangular pyramid to	
O(4)-Ge(2)-O(7)	102.1(3)	O(5) atom)	
O(6)-Ge(2)-O(7)	109.4(3)		
		O(5)	2.416(8)
Ge(1)-O(7)-Ge(2)	127.0(2)	O(10)	2.830(5)
Germanium (3)		Pb(4)^F	
O(8)	1.741(5)		
O(9)	1.750(6)	O(6)	2.445(9)
O(10)	1.716(6)	O(9)	2.716(7)
O(11)	1.795(6)		
		Pb(5)^F Triangular pyramid to	
O(8)-Ge(3)-O(9)	112.5(5)	O(3) and O(4)	
O(8)-Ge(3)-O(10)	114.1(4)		

O(8)-Ge(3)-O(11)	109.1(3)	O(3)	2.524(8)
O(9)-Ge(3)-O(10)	110.5(3)	O(4)	2.831(7)
O(9)-Ge(3)-O(11)	106.8(3)		
O(10)-Ge(3)-O(11)	103.1(3)	$Pb(6)^F$ (Triangular prism to O(5) and O(6)	
$Pb(7)^T$ (Triangular pyramid to oxygen 1, 3, 10)		O(5)	2.459(8)
		O(6)	2.448(8)
O(1)	2.277(6)		
O(3)	2.277(6)	$Pb(9)^T$ (Pentagonal pyramid)	
O(5)	2.986(6)		
O(10)	2.195(5)	O(9)	2.183(6)
		O(2)	2.461(6)
O(1)-Pb(7)-O(3)	82.6(2)	O(11)	2.534(6)
O(1)-Pb(7)-O(10)	93.4(2)	O(8)	2.688(5)
O(3)-Pb(7)-O(10)	92.3(2)	O(1)	2.837(6)

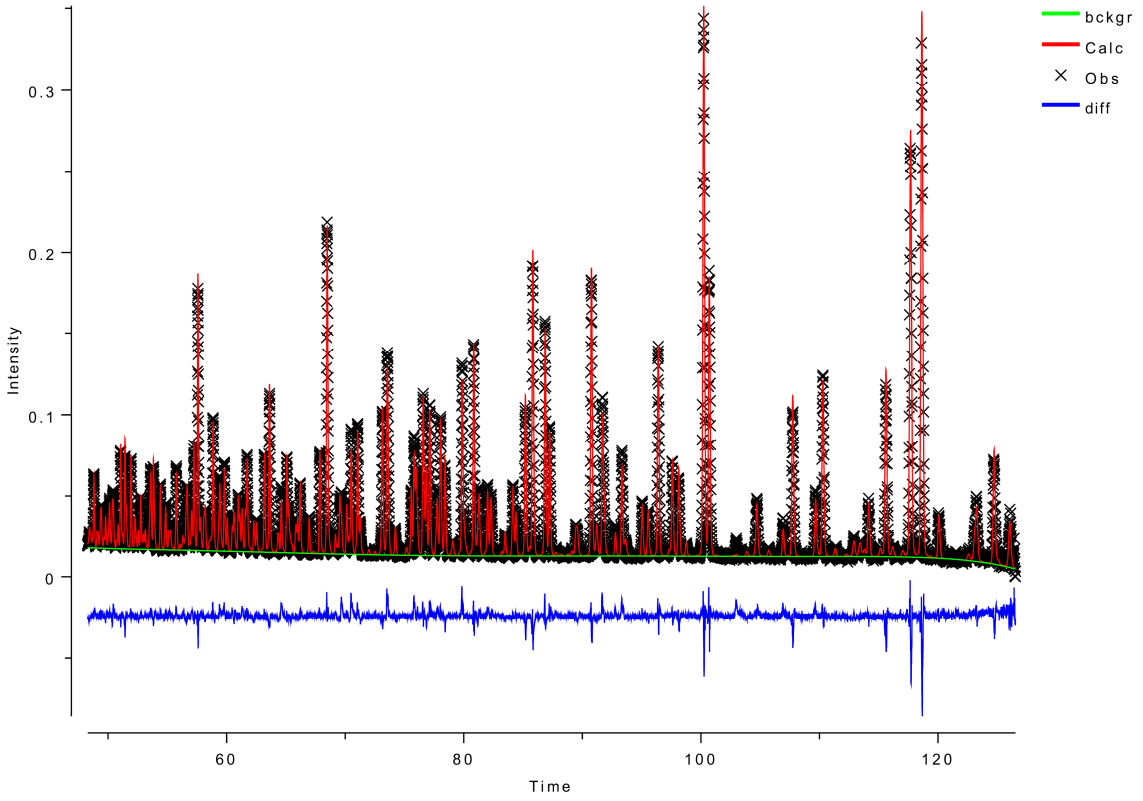

Figure S1b. TOF neutron diffraction profile for $Pb_{15}(Ge_2O_7)_3(GeO_4)_3$ in $P\bar{6}$

Table S1c. Refined crystal data for ganomalite, $Pb_{15}(Ge_2O_7)_3(GeO_4)_3$ in $P\bar{6}$

S.G.	$P\bar{6}$	$a = 10.22887(1)$ Å	$c = 10.66337(2)$ Å	$wRp = 0.066$ $R_F = 0.074$

Site	x	y	z	$100 \times U_{Iso}$
Pb(1)^{F}	1/3	2/3	0.3270(4)	0.2(1)
Pb(2)^{F}	2/3	1/3	0.3390(4)	0.2(1)
Pb(3)^{F}	1/3	2/3	0	1.1(2)
Pb(4)^{F}	2/3	1/3	0	2.2(2)
Pb(5)^{T}	0.2578(3)	0.0076(4)	0.5	1.19(8)
Pb(6)^{T}	-0.0026(3)	0.7343(2)	0.1847(1)	0.52(4)
Ge(1)	0.3940(3)	0.0164(3)	0.1521(2)	0.46(6)
Ge(2)	0.0049(5)	0.6122(4)	0.5	-0.93(7)
O(1)	0.0774(4)	0.7283(4)	0.6305(3)	1.4(1)
O(2)	0.4801(4)	0.2894(4)	0.5	-1.71(9)
O(3)	0.0711(9)	0.4910(9)	0.5	6.4(3)
O(4)	0.5133(4)	0.4059(4)	0.1608(3)	1.48(9)
O(5)	0.1812(4)	0.4962(5)	0.1664(4)	2.5(1)
O(6)	0.3659(4)	0.0710(5)	0.0	0.5(1)
O(7)	0.3203(3)	0.0916(3)	0.2623(2)	0.08(6)

Table S1d. Refined bond lengths for the isolated Ge(2)-O_4 tetrahedra in the space group $P\bar{6}$

Bond	Distance
Ge(2) – O(1)	1.737(4)
Ge(2) – O(2)	1.734(5)
Ge(3) – O(3)	1.683(10)

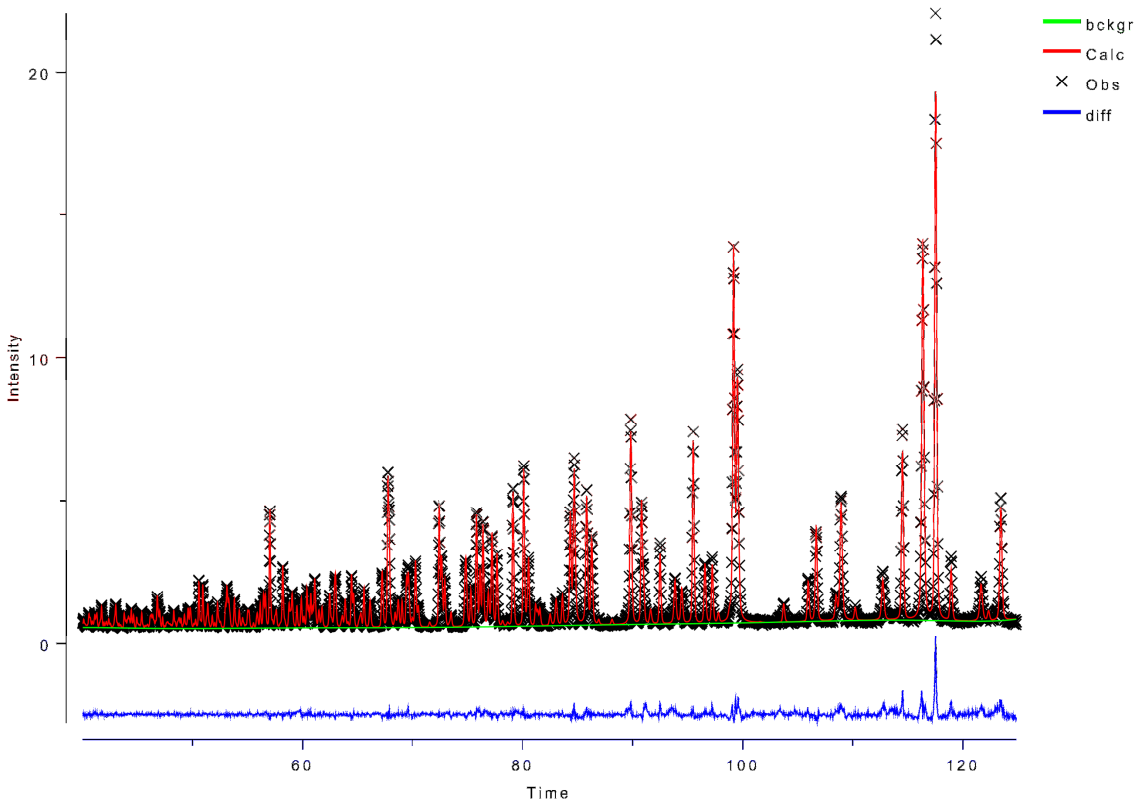

Figure S2. TOF neutron diffraction profile for $Bi_{1.5}Na_{1.5}Pb_{12}(Ge_2O_7)_3(GeO_4)_3$.

Table S2a. Refined crystal data for $Bi_{1.5}Na_{1.5}Pb_{12}(Ge_2O_7)_3(GeO_4)_3$.

S.G.	*P*3	a = 10.13385(3) Å	c = 10.52045(6) Å	wRp = 0.040 R_F =0.040
Site	***x***	***y***	***z***	**100 × U_{Iso}**

***A*(1)^F**	1/3	2/3	0.312(2)	2.5(2)
***A*(2)^F**	1/3	2/3	0.646(2)	0.9(1)
***A*(3)^F**	2/3	1/3	0.301(2)	2.7(2)
***A*(4)^F**	2/3	1/3	0.674(2)	2.4(2)
***A*(5)^F**	1/3	2/3	0.997*	0.8(1)
***A*(6)^F**	2/3	1/3	-0.012(4)	2.5(2)
***A*(7)^T**	0.2593(7)	0.2603(8)	0.170(2)	1.7(2)
***A*(8)^T**	0.2632(8)	0.2633(9)	0.809(2)	2.4(2)
***A*(9)^T**	0.2483(4)	0.9970(5)	0.493(2)	2.3(2)
Ge(1)	0.0079(9)	0.3903(8)	0.142(2)	2.3(2)
Ge(2)	0.0170(8)	0.3971(8)	0.837(2)	1.3(1)
Ge(3)	0.3963(4)	0.3910(5)	0.489(2)	1.6(2)
O(1)	0.0811(4)	0.3118(10)	0.249(2)	3.5(3)
O(2)	0.0870(12)	0.3291(9)	0.722(2)	1.8(2)
O(3)	0.0993(11)	0.5951(13)	0.144(2)	2.9(3)
O(4)	0.1210(11)	0.5962(13)	0.820(2)	1.8(2)
O(5)	0.8211(14)	0.3167(14)	0.151(2)	2.0(2)
O(6)	0.8168(10)	0.3171(11)	0.838(2)	2.3(2)
O(7)	0.0706(5)	0.3573(5)	0.989(2)	4.1(3)
O(8)	0.2858(6)	0.4807(6)	0.493(2)	2.6(3)
O(9)	0.5931(8)	0.5079(8)	0.514(2)	1.8(2)
O(10)	0.3706(11)	0.2766(12)	0.357(2)	2.7(3)
O(11)	0.3313(9)	0.2558(10)	0.613(2)	3.3(3)

Table S2b. Pb, Bi and Na site distribution for $Bi_{1.5}Na_{1.5}Pb_{12}(Ge_2O_7)_3(GeO_4)_3$.

Site	**Pb**	**Na**	**Bi**
***A*(1)^F**	0.893	0.107	0.000
***A*(2)^F**	0.844	0.156	0.000
***A*(3)^F**	0.469	0.062	0.469
***A*(4)^F**	0.468	0.065	0.467
***A*(5)^F**	0.000	0.607	0.393
***A*(6)^F**	0.000	0.522	0.478
***A*(7)^T**	1.000	0.000	0.000
***A*(8)^T**	1.000	0.000	0.000
***A*(9)^T**	1.000	0.000	0.000

Table S2c. Selected bond distances and angles for $Bi_{1.5}Na_{1.5}Pb_{12}(Ge_2O_7)_3(GeO_4)_3$.

Ge-O tetrahedra			
Germanium (1)	Distance or Angle	$A(8)^T$	
O(1)	1.75(1)	O(2)	2.38(1)
O(3)	1.80(1)	O(4)	2.30(1)
O(5)	1.65(1)	O(6)	2.91(2)
O(7)	1.82(2)	O(11)	2.19(1)
O(1)-Ge(1)-O(3)	115.2(6)	O(2)-Pb(8)-O(4)	79.4(4)
O(1)-Ge(1)-O(5)	114.1(8)	O(2)-Pb(8)-O(11)	86.5(5)
O(1)-Ge(1)-O(7)	102.7(6)	O(4)-Pb(8)-O(11)	93.5(4)
O(3)-Ge(1)-O(5)	109.4(7)		
O(3)-Ge(1)-O(7)	101.4(6)	$A(1)^F$ (Triangular pyramid to 3	
O(5)-Ge(1)-O(7)	113.2(8)	equivalent O(8) atoms)	
Germanium (2)		O(8)	2.55(2)
O(2)	1.71(1)	O(3)	2.75(1)
O(4)	1.76(1)		
O(6)	1.77(1)	$A(2)^F$	
O(7)	1.80(2)		
		O(8)	2.34(1)
O(2)-Ge(2)-O(4)	104.9(6)	O(4)	2.64(1)
O(2)-Ge(2)-O(6)	115.4(7)		
O(2)-Ge(2)-O(7)	107.9(6)	$A(3)^F$ (Triangular pyramid to	
O(4)-Ge(2)-O(6)	114.8(6)	O(5) atom)	
O(4)-Ge(2)-O(7)	105.9(6)		
O(6)-Ge(2)-O(7)	107.4(6)	O(5)	2.29(2)
		O(10)	2.82(1)
Ge(1)-O(7)-Ge(2)	124.9(3)		
		$A(4)^F$	
Germanium (3)			
O(8)	1.761(7)	O(4)	2.36(2)
O(9)	1.756(8)	O(9)	2.80(1)
O(10)	1.74(2)		
O(11)	1.76(1)	$A(5)^F$ (Triangular pyramid to	
		O(3) and O(4))	
O(8)-Ge(3)-O(9)	116.7(4)		
O(8)-Ge(3)-O(10)	116.1(8)	O(3)	2.61(2)
O(8)-Ge(3)-O(11)	107.2(6)	O(4)	2.67(2)
O(9)-Ge(3)-O(10)	107.9(6)		
O(9)-Ge(3)-O(11)	105.8(6)	$A(6)^F$ (Triangular prism to	
O(10)-Ge(3)-O(11)	101.5(4)	O(5) and O(6)	
		O(5)	2.38(3)
$A(7)^T$		O(6)	2.26(3)
(Triangular pyramid to oxygen 1, 3,10)			
O(1)	2.27(2)	$A(9)^T$ (Trigonal prism)	
O(3)	2.17(1)		
O(5)	2.90(1)	O(9)	2.178(8)
O(10)	2.23(1)	O(2)	2.55(2)
		O(11)	2.65(1)
O(1)-Pb(7)-O(3)	87.2(4)	O(8)	2.637(7)
O(1)-Pb(7)-O(10)	95.1(5)	O(1)	2.66(2)
O(3)-Pb(7)-O(10)	89.8(5)	O(10)	2.84(1)

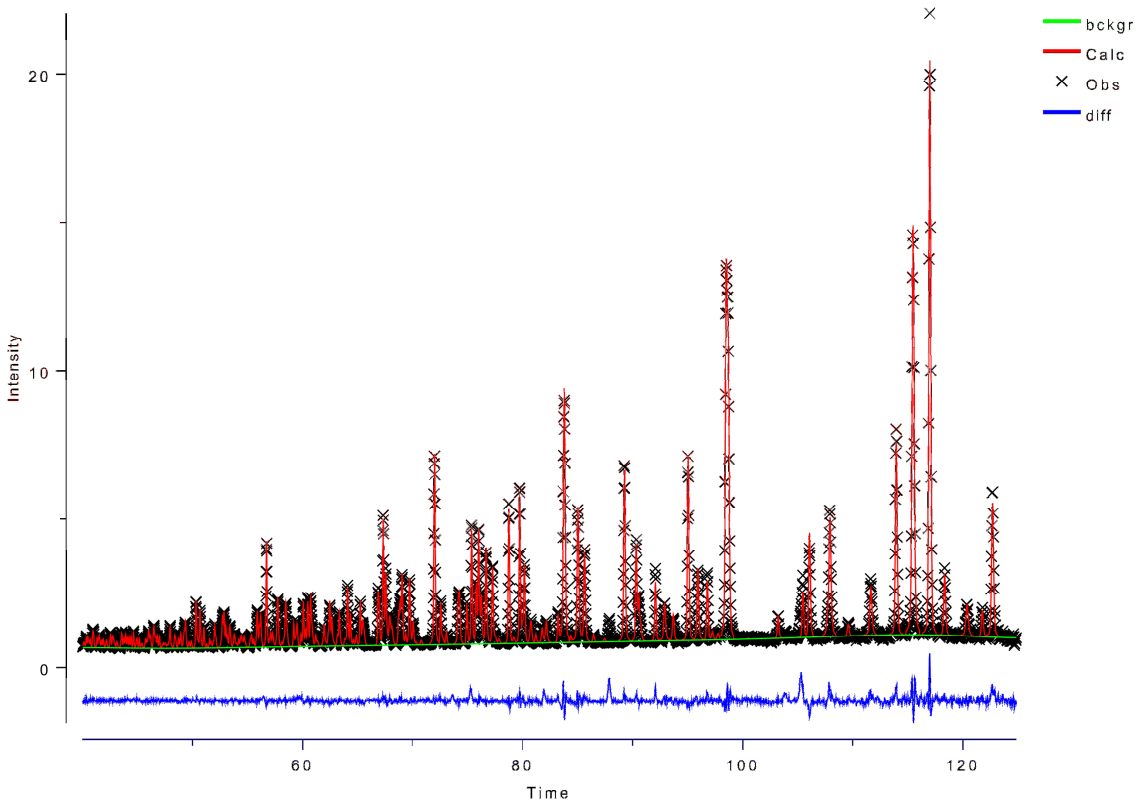

Figure S3. TOF neutron diffraction profile for $Bi_3Na_3Pb_9(Ge_2O_7)_3(GeO_4)_3$.

Table S3a. Refined crystal data for $Bi_3Na_3Pb_9(Ge_2O_7)_3(GeO_4)_3$.

S.G.	*P*3	*a* = 10.08745(3) Å	*c* = 10.40506(7) Å	*wRp* = 0.045 R_F = 0.053
Site	***x***	***y***	***z***	**100 × U_{Iso}**
***A*(1)^F**	1/3	2/3	0.326(5)	2.5(2)
***A*(2)^F**	1/3	2/3	0.643(6)	2.3(2)
***A*(3)^F**	2/3	1/3	0.296(5)	3.2(3)
***A*(4)^F**	2/3	1/3	0.684(5)	1.7(1)
***A*(5)^F**	1/3	2/3	0.997*	3.5(3)
***A*(6)^F**	2/3	1/3	-0.034(6)	3.2(3)
***A*(7)^T**	0.2648(9)	0.2666(10)	0.167(5)	1.7(2)
***A*(8)^T**	0.2574(10)	0.2621(11)	0.810(5)	1.6(2)
***A*(9)^T**	0.2443(5)	0.9969(7)	0.489(5)	2.5(2)
Ge(1)	0.0127(12)	0.3971(12)	0.142(5)	2.1(2)
Ge(2)	0.0169(13)	0.3959(12)	0.833(5)	1.7(2)
Ge(3)	0.3994(6)	0.3932(6)	0.486(5)	1.4(2)
O(1)	0.0707(14)	0.2950(10)	0.248(5)	2.5(2)
O(2)	0.0888(15)	0.3331(13)	0.718(5)	2.1(2)

O(3)	0.1185(22)	0.5971(22)	0.165(5)	4.4(4)
O(4)	0.1158(18)	0.6002(18)	0.830(5)	3.3(3)
O(5)	0.8245(14)	0.3306(15)	0.150(5)	2.2(2)
O(6)	0.8128(16)	0.3126(16)	0.831(5)	2.6(3)
O(7)	0.0677(7)	0.3550(7)	0.989(6)	2.3(2)
O(8)	0.2906(8)	0.4852(7)	0.491(6)	2.7(3)
O(9)	0.5961(9)	0.5108(10)	0.514(5)	2.9(3)
O(10)	0.3751(17)	0.2795(16)	0.354(5)	4.1(4)
O(11)	0.3334(16)	0.2534(16)	0.609(5)	2.9(3)

Table S3b. Pb, Bi and Na site distribution for $Bi_3Na_3Pb_9(Ge_2O_7)_3(GeO_4)_3$.

Site	Pb	Na	Bi
$A(1)^F$	0.320	0.173	0.507
$A(2)^F$	0.000	0.323	0.677
$A(3)^F$	0.000	0.198	0.802
$A(4)^F$	0.000	0.253	0.747
$A(5)^F$	0.000	0.726	0.274
$A(6)^F$	0.000	1.000	0.000
$A(7)^T$	0.995	0.005	0.000
$A(8)^T$	0.901	0.099	0.000
$A(9)^T$	0.975	0.015	0.000

Table S3c. Selected bond distances and angles for $Bi_3Na_3Pb_9(Ge_2O_7)_3(GeO_4)_3$.

Ge-O tetrahedra			
Germanium (1)	Distance or Angle	$A(8)^T$	
O(1)	1.79(2)	O(2)	2.35(2)
O(3)	1.77(2)	O(4)	2.23(2)
O(5)	1.67(2)	O(6)	2.91(2)
O(7)	1.80(2)	O(11)	2.24(1)
O(1)-Ge(1)-O(3)	112.9(9)	O(2)-Pb(8)-O(4)	80.7(5)
O(1)-Ge(1)-O(5)	111.8(9)	O(2)-Pb(8)-O(11)	86.9(5)
O(1)-Ge(1)-O(7)	100.4(7)	O(4)-Pb(8)-O(11)	95.6(6)
O(3)-Ge(1)-O(5)	111.6(9)		
O(3)-Ge(1)-O(7)	107.9(8)	$A(1)^F$ (Triangular pyramid to 3	
O(5)-Ge(1)-O(7)	111.7(9)	equivalent O(8) atoms)	
Germanium (2)		O(8)	2.39(2)
		O(3)	2.55(2)
O(2)	1.68(2)		
O(4)	1.79(2)	$A(2)^F$	
O(6)	1.79(2)		
O(7)	1.82(2)	O(8)	2.29(3)
		O(4)	2.76(3)

		$A(3)^F$ (Triangular pyramid to	
O(2)-Ge(2)-O(4)	109.1(9)	O(5) atom)	
O(2)-Ge(2)-O(6)	115.4(10)		
O(2)-Ge(2)-O(7)	109.3(7)	O(5)	2.21(2)
O(4)-Ge(2)-O(6)	112.9(8)	O(10)	2.78(2)
O(4)-Ge(2)-O(7)	102.6(8)		
O(6)-Ge(2)-O(7)	106.8(9)	$A(4)^F$	
Ge(1)-O(7)-Ge(2)	125.7(4)	O(6)	2.21(2)
		O(9)	2.85(2)
Germanium (3)			
O(8)	1.76(1)	$A(5)^F$ Triangular pyramid to	
O(9)	1.75(1)	O(3) and O(4)	
O(10)	1.72(2)		
O(11)	1.77(2)	O(3)	2.59(4)
		O(4)	2.61(4)
O(8)-Ge(3)-O(9)	115.6(5)		
O(8)-Ge(3)-O(10)	117.5(10)	$A(6)^F$ (Triangular prism to O(5)	
O(8)-Ge(3)-O(11)	108.1(9)	and O(6)	
O(9)-Ge(3)-O(10)	108.6(8)		
O(9)-Ge(3)-O(11)	105.4(8)	O(5)	2.50(3)
O(10)-Ge(3)-O(11)	99.8(6)	O(6)	2.12(3)
$A(7)^T$		$A(9)^T$ (Trigonal prism)	
(Triangular pyramid to oxygen 1, 3, 10)			
		O(9)	2.18(2)
O(1)	2.28(2)	O(2)	2.53(2)
O(3)	2.23(2)	O(11)	2.59(2)
O(5)	3.01(2)	O(8)	2.68(1)
O(10)	2.22(2)	O(1)	2.58(2)
		O(10)	2.84(2)
O(1)-Pb(7)-O(3)	86.5(6)		
O(1)-Pb(7)-O(10)	96.1(5)		
O(3)-Pb(7)-O(10)	86.2(7)		

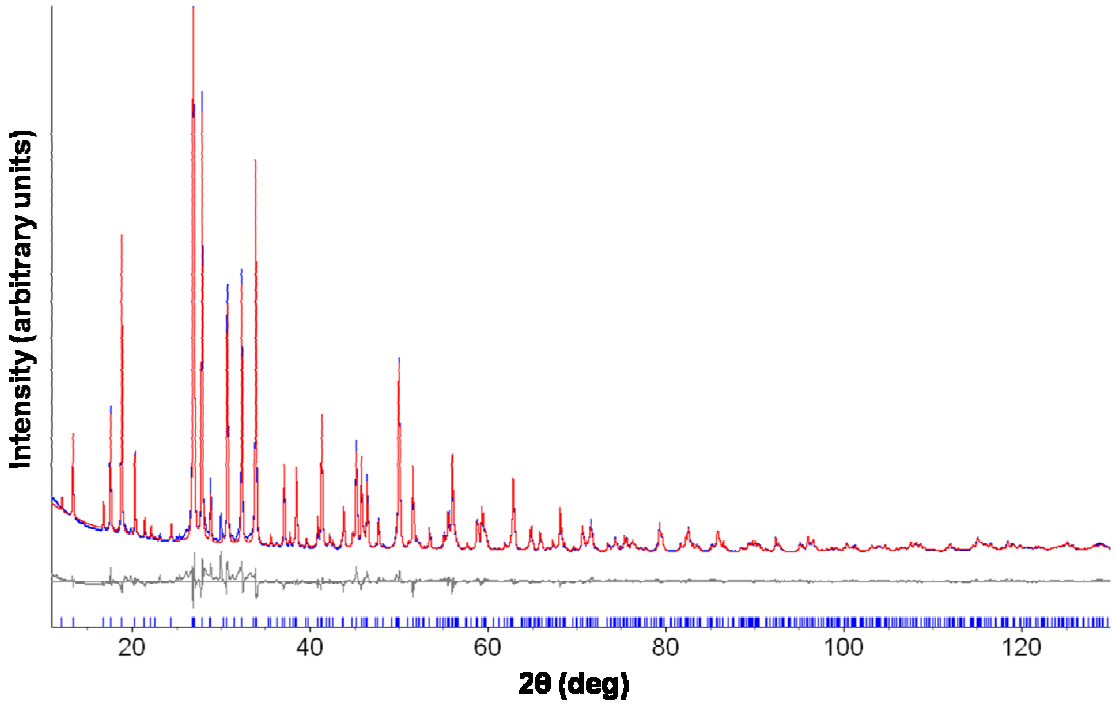

Figure S4. XRD diffraction profile for $Ca_8Pb_{12}(Si_2O_7)_6Cl_4$

Table S4a. Refined crystal data for nasonite, $Ca_8Pb_{12}(Si_2O_7)_6Cl_4$ from neutron TOF data.

S.G.	$P6_3/m$	a = 10.0898(1) Å	c = 13.2506(2) Å	wR_p = 0.059	R_F = 0.070
Site	***x***	***y***	***z***	**100 × U_{Iso}**	**Occ.**
Ca(1)^F	1/3	2/3	0.9953(6)	2.0(2)	1
Ca(2)^F	1/3	2/3	0.25	2.5(2)	1
Ca(3)^F	2/3	1/3	0.25	1.5(2)	1
Pb(1)^T	0.2475(2)	0.2660(2)	0.1085(1)	2.7(3)	1
Si(1)	0.0253(4)	0.4185(4)	0.3639(3)	2.5(2)	1
O(1)	0.0774(4)	0.3300(4)	0.4442(2)	2.5(2)	1
O(2)	0.8606(3)	0.3956(3)	0.6206(2)	2.6(3)	1
O(3)	0.8508(3)	0.3702(3)	0.3709(2)	2.4(2)	1
O(4)	0.0718(5)	0.3823(5)	0.25	2.7(3)	1
O(5)	0	0	0.181(6)	2.5(2)	0.025
Cl(1)	0	0	0.242(1)	2.1(2)	0.45(1)
Cl(2)	0	0	-0.009(1)	2.7(2)	0.50(1)

Table S4b. Selected bond distances and angles for nasonite, $Ca_8Pb_{12}(Si_2O_7)_6Cl_4$

Atoms	Distance (Å)	Atoms	Distance (Å)
Si-O(1)	1.635(5)	**Pb(1)-O(1)**	2.319(4), 2.322(4)
Si-O(2)	1.651(5)	**Pb(1)-O(2)**	2.357(3)
Si-O(3)	1.578(5)		
Si-O(4)	1.674(4)		
		Atoms	**Angle (°)**
Ca(1)-O(2)	2.397(6)		
Ca(1)-O(3)	2.370(6)		
Ca(2)-O(2)	2.436(3)	**O(1)-Si-O(2)**	107.9(2)
Ca(2)-O(4)	2.761(4)	**O(1)-Si-O(3)**	114.0(3)
		O(1)-Si-O(4)	105.4(3)
Pb(1)-Cl(1)	3.175(10)	**O(2)-Si-O(3)**	112.3(3)
	3.306(11)	**O(2)-Si-O(4)**	104.4(3)
		O(3)-Si-O(4)	112.2(3)
Pb(1)-Cl(2)	3.065(8)		
	2.954(7)	**Si-O(4)-Si**	128.8(4)