Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Local Structure in a Tetravalent-Substituent BIMEVOX system: BIGEVOX

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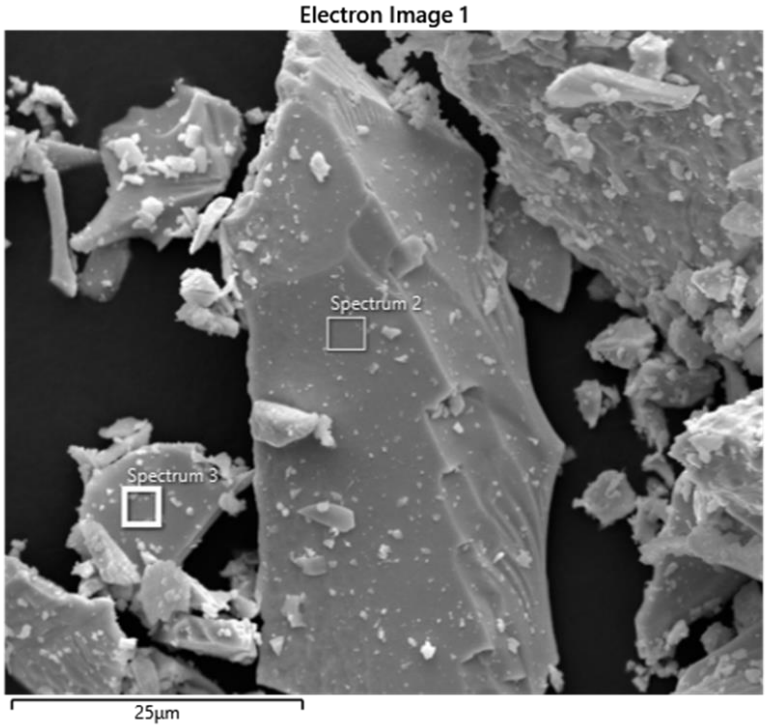

Fig. S1 SEM image of $Bi_2V_{0.65}Ge_{0.35}O_{5.325}$ powder used for EDX analysis.

Table S1 Comparison of theoretical and average EDX analysis values for consituent elements in $Bi_2V_{0.65}Ge_{0.35}O_{5.325}$.

	Bi	V	Ge	O
EDX analysis	23.61 %	7.67 %	4.43 %	63.30 %
Theoretical	24.02 %	7.81 %	4.20 %	63.96 %

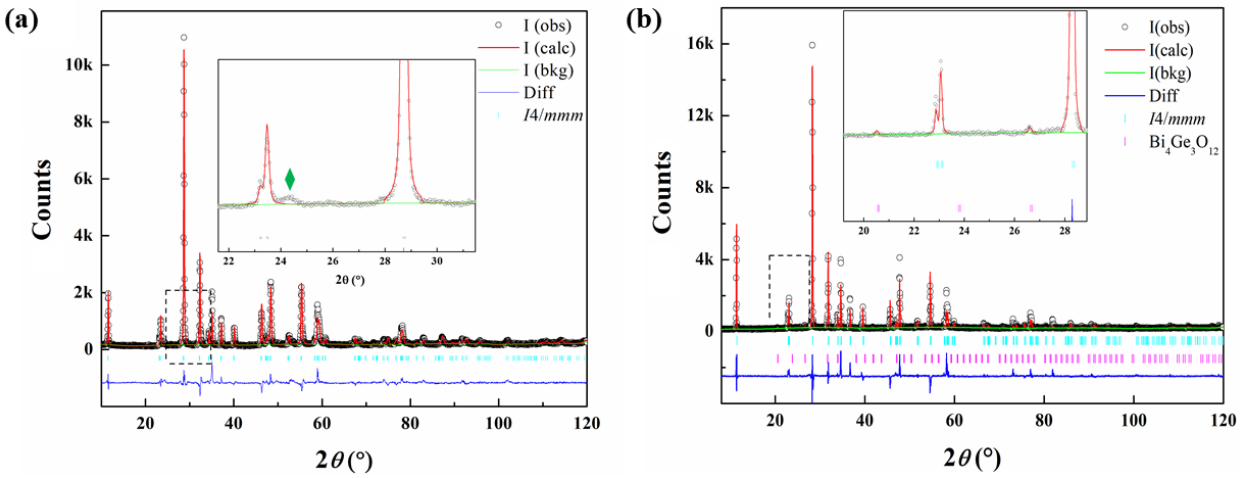

Fig. S2. Fitted diffraction profiles for BIGEVOX35 at room temperature showing fits to XRD data at (a) 25 °C and (b) 700 °C. The insets show the variation of a superlattice peak at *ca*. 24.2° 2θ at the two studied temperatures.

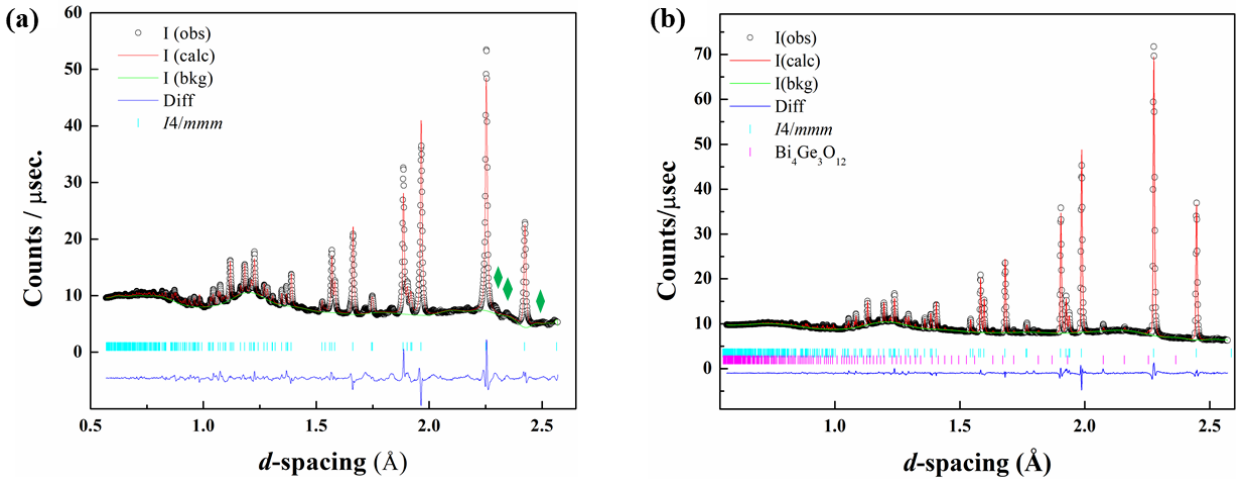

Fig. S3. Fitted diffraction profiles for BIGEVOX35 at room temperature showing fits to neutron back-scattering data at (a) 25 °C and (b) 700 °C. The green symbols mark a set of superlattice peak observed at 25 °C due to the incommensurate modulation of the γ′-phase.

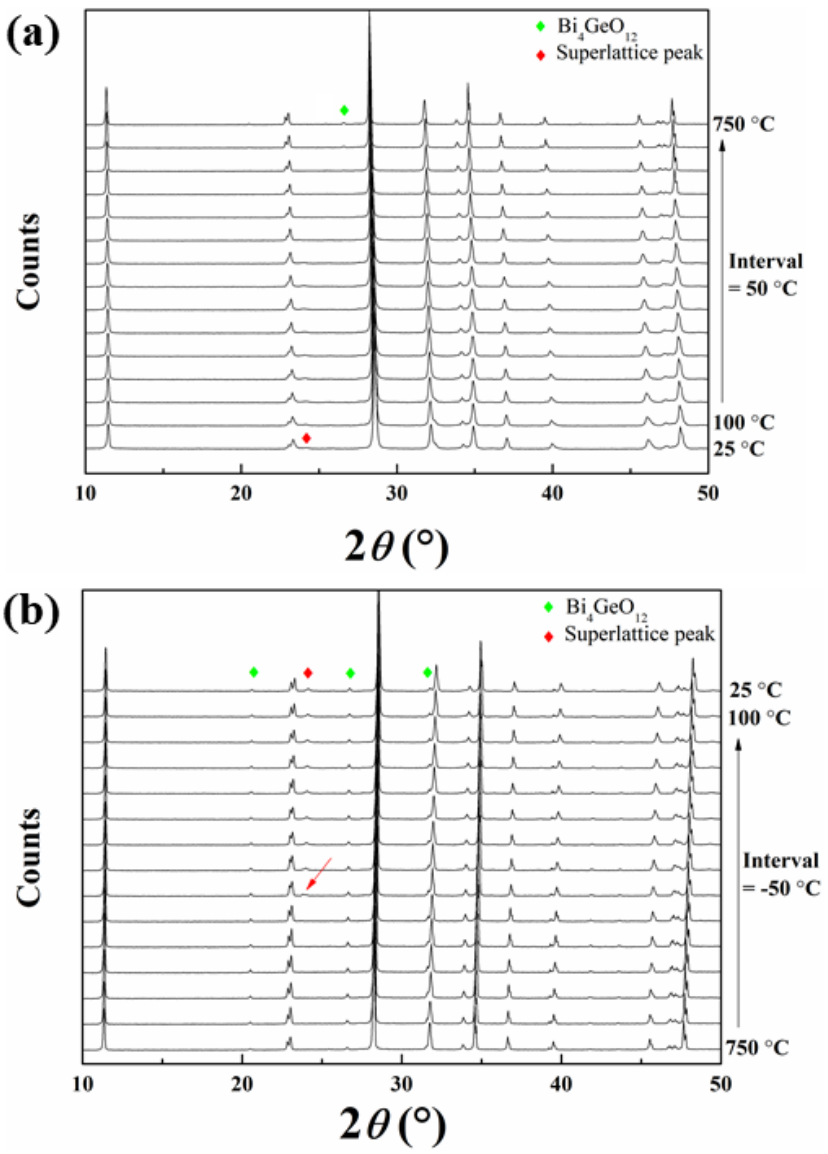

Fig. S4. Thermal variation of X-ray diffraction patterns for BIGEVOX35 on heating and cooling between 25 °C and 750 °C.

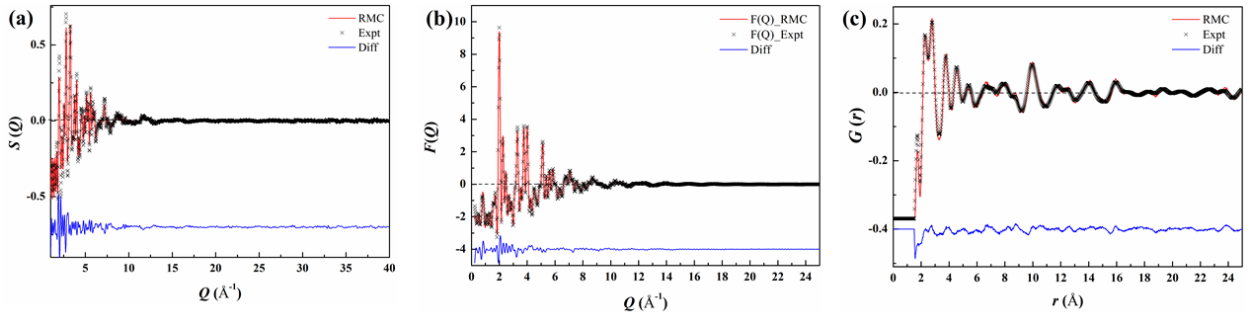

Fig. S5. Representative fitted profiles for BIGEVOX35 at 25 °C derived from RMC calculations showing (a) neutron $S(Q)$, (b) X-ray $F(Q)$ and (c) $G(r)$.

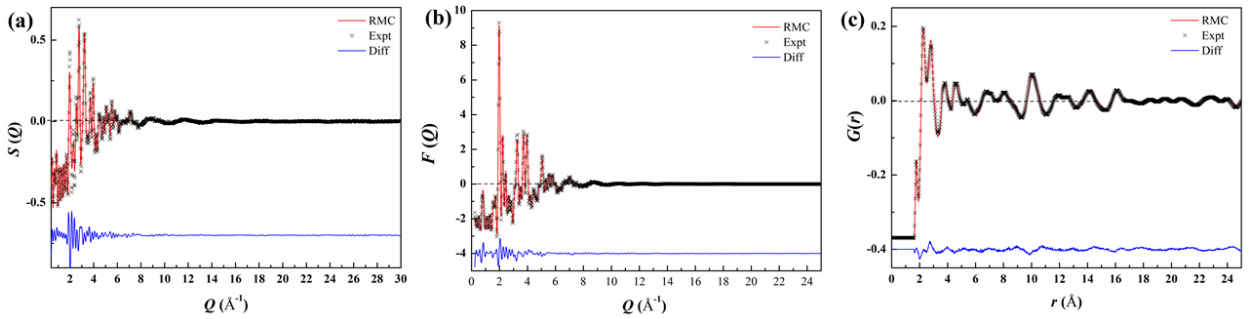

Fig. S6. Representative fitted profiles for BIGEVOX35 at 700 °C derived from RMC calculations showing (a) neutron $S(Q)$, (b) X-ray $F(Q)$ and (c) $G(r)$.

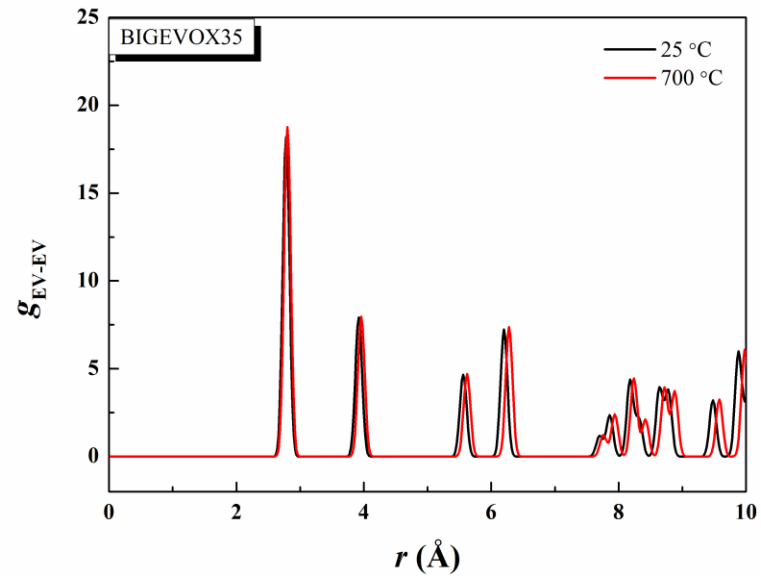

Fig. S7. Partial PDFs for EV-EV pairs in BIGEVOX35 at 25 and 700 °C. For clarity, the distribution functions at the two temperatures are smoothed over 10 cycles.

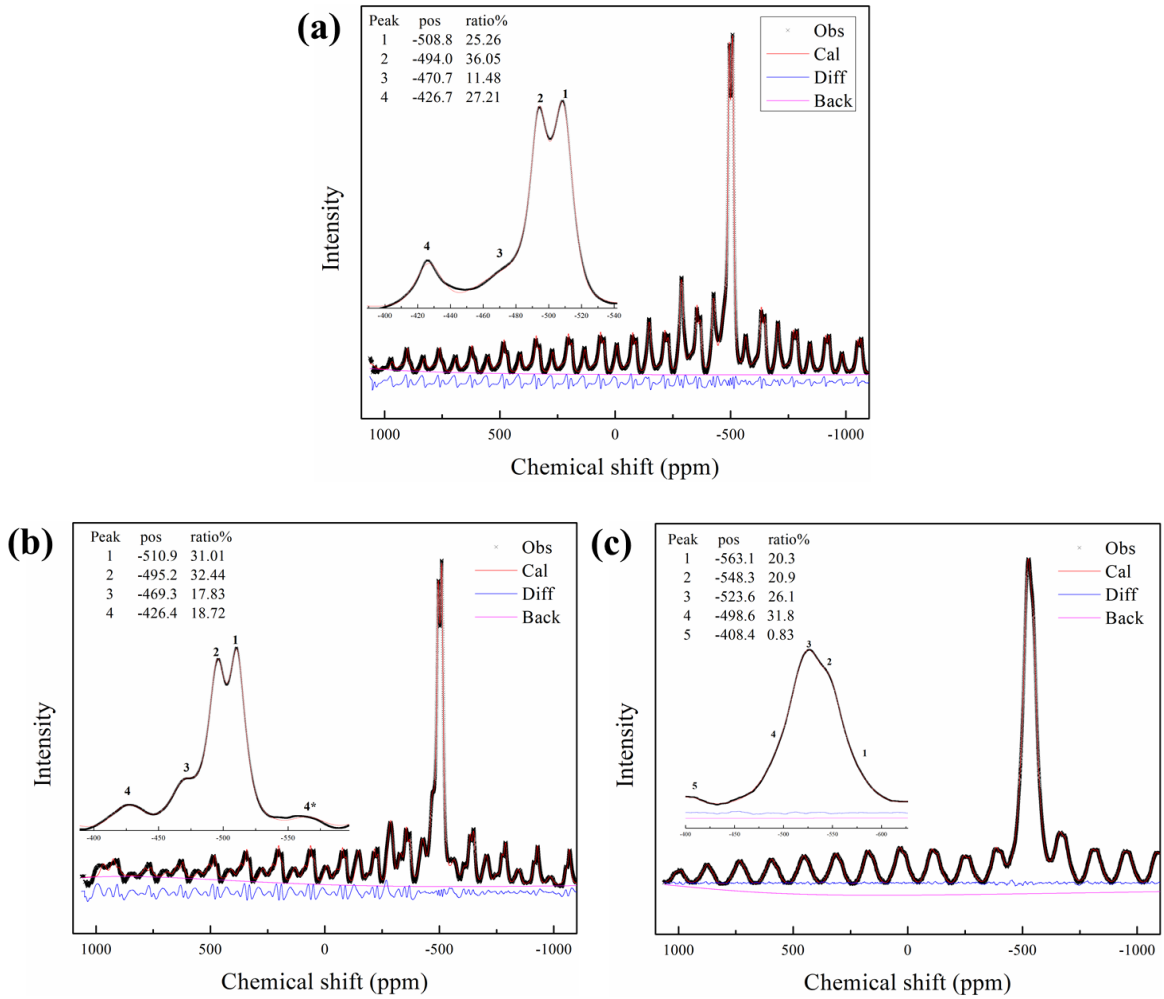

Fig. S8. Fitted ^{51}V solid-state NMR spectra for $Bi_2V_{1-x}Ge_xO_{5.5-0.5x-\delta}$ compositions: (a) x = 0.0, (b) x = 0.05, and (c) x = 0.35.

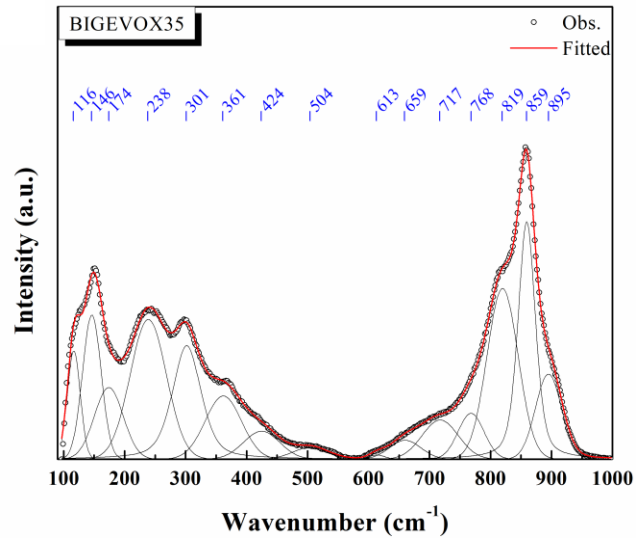

Fig. S9. Fitted Raman spectrum for BIGEVOX35 at room temperature.

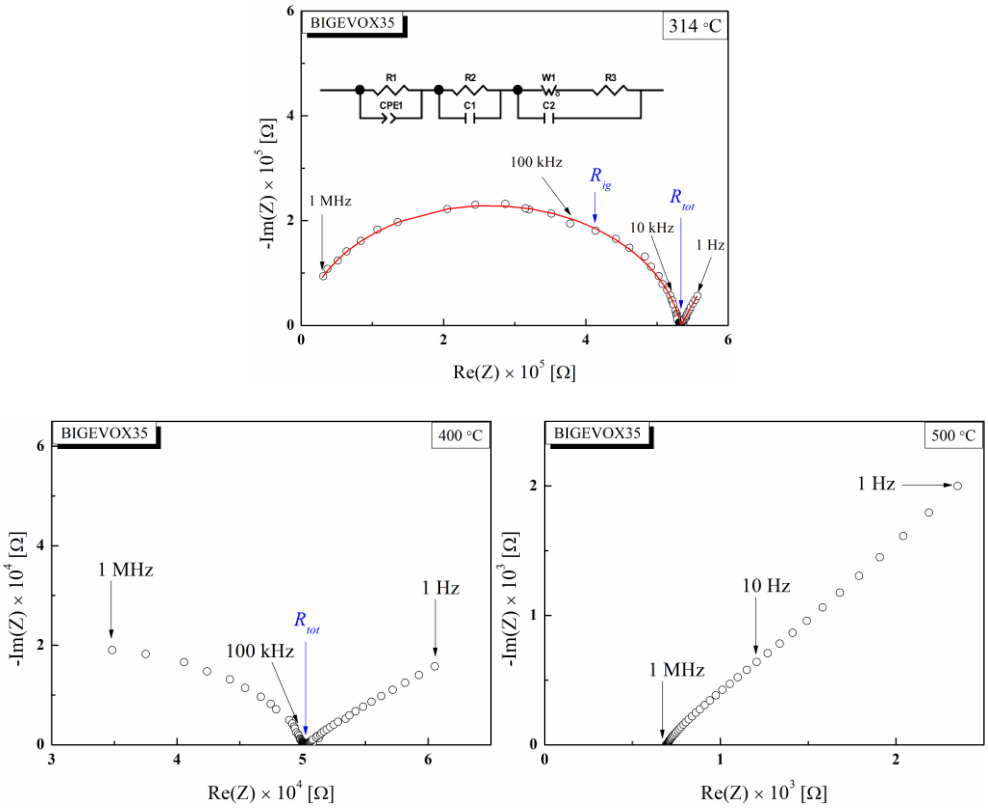

Fig. S10. Typical Nyquist plots at selected temperatures (314, 400 and 500 °C) for $Bi_2V_{0.65}Ge_{0.35}O_{5.325}$, with fits shown at 314 °C. The equivalent circuit used is shown inset, which consists of resistors *R*, capacitors *C*, and constant phase elements *CPE* to model intragrain (*ig*), and intergrain (*gb*) dispersions.

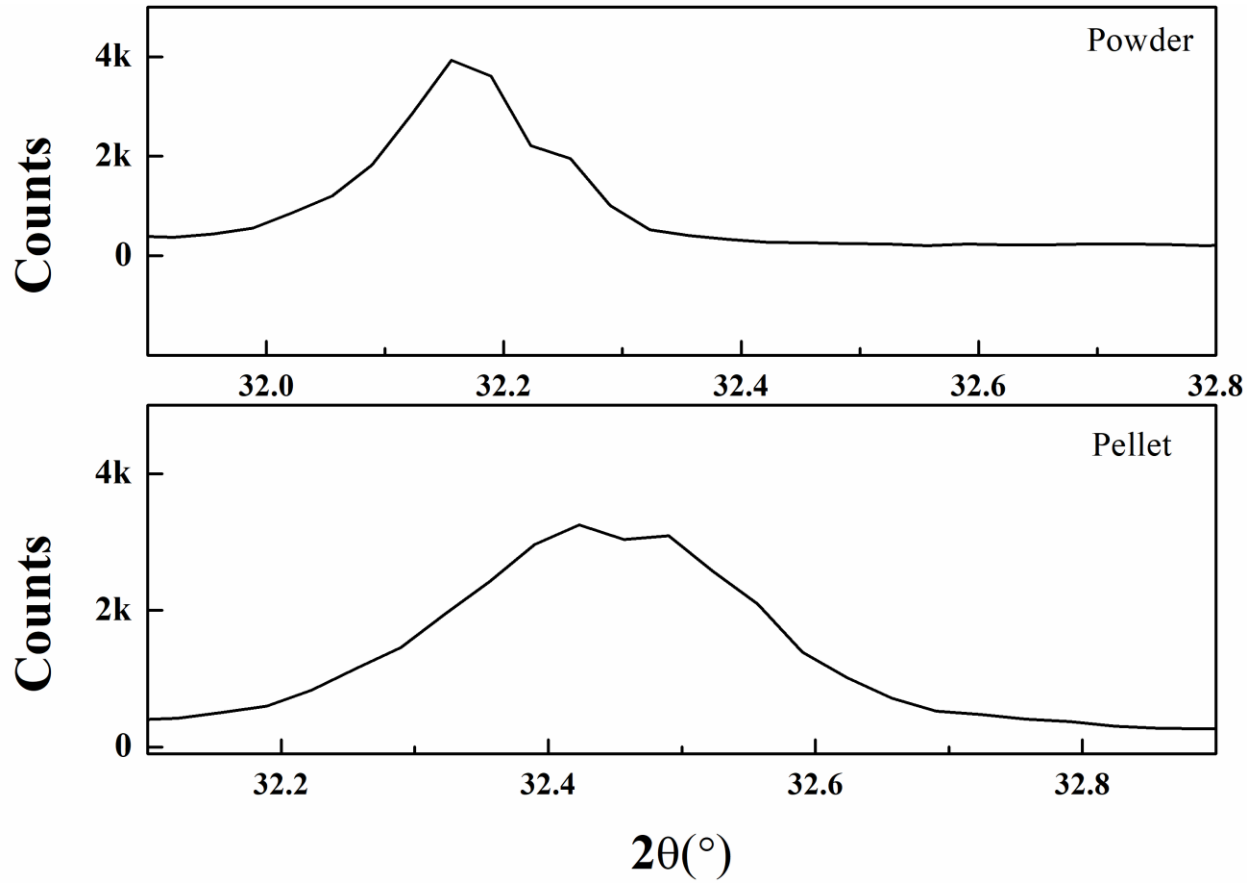

Fig. S11. Detail of room temperature X-ray powder diffraction patterns for BIGEVOX35 prepared as powder (upper) and ceramic pellet (lower) showing (200)/(020) mean cell peaks.

Table S2. Thermal expansion coefficients for BIGEVOX35 at low and high temperatures.

Temp. region	Thermal expansion coefficient, α ($°C^{-1}$)		
	a-axis	*c*-axis	Cell volume
LT (< 500 °C)	1.82×10^{-5}	1.67×10^{-3}	2.26×10^{-3}
HT (≥ 500 °C)	1.52×10^{-5}	3.84×10^{-3}	4.80×10^{-3}

Table S3. Crystal and refinement parameters for BIGEVOX35 at 25 ˚C and 700 ˚C.

Sample Name		BIGEVOX35		
Temperature (°C)		20 °C	700 °C	
			Phase 1	Phase 2
Chemical formula		$Bi_2V_{0.65}Ge_{0.35}O_{5.325}$	$Bi_2V_{0.65}Ge_{0.35}O_{5.325}$	$Bi_4Ge_3O_{12}$
Crystal system		*I* 4/*mmm*	*I* 4/*mmm*	*I* -43*d*
Phase fraction		100%	98.52(3)%	1.47(7)%
Lattice parameter(s) (Å)		*a* = 3.9268(4) *c* = 15.387(1)	*a* = 3.9718(1) *c* = 15.5183(4)	*a* = 10.574(1)
Volume ($Å^3$)		237.27(7)	244.80(2)	1182.3(4)
Z		2	2	4
Density (calc) g cm^{-3}		7.862	7.619	6.998
R-factors	Neutron back scattering	R_{wp} = 0.0183 R_p = 0.0267 R_{ex} = 0.0037 R_F^2 = 0.1149	R_{wp} = 0.0088 R_p = 0.0118 R_{ex} = 0.0037 R_F^2 = 0.1509	
	Neutron 90°	R_{wp} = 0.0218 R_p = 0.0283 R_{ex} = 0.0022 R_F^2 = 0.1402	R_{wp} = 0.0100 R_p = 0.0133 R_{ex} = 0.0022 R_F^2 = 0.1351	
	X-ray	R_{wp} = 0.1326 R_p = 0.0952 R_{ex} = 0.0607 R_F^2 = 0.2268	R_{wp} = 0.1563 R_p = 0.1126 R_{ex} = 0.0607 R_F^2 = 0.3544	
	Totals	R_{wp} = 0.0212 R_p = 0.0845	R_{wp} = 0.0114 R_p = 0.0899	
No. of variables		119	131	
χ^2		32.86	9.416	
No. of profile points	Neut. (bs) (90 °C) X-ray	3020 1827 3290	3025 1827 3348	

Table S4. Refined atomic parameters for BIGEVOX35 at 25 °C and 700 °C.

25 ˚C						
Atom	Site	*x*	*y*	*z*	Occ.	U_{iso} (Å^2)
Bi	4e	0.0	0.0	0.16816(6)	1.0	0.0346(5)
M (V/Ge)	2b	0.5	0.5	0.0	0.65/0.35	0.045(1)
O(1)	4d	0.0	0.5	0.25	1.0	0.0260(5)
O(2)	4e	0.5	0.5	0.1020(3)	0.337(5)	0.048(1)
O(3)	32e	0.549(1)	0.079(1)	0.0343(2)	0.0828	0.038(1)
O(4)	16n	0.5	0.0279(1)	0.0891(3)	0.166(1)	0.048(1)
700 ˚C						
Atom	Site	*x*	*y*	*z*	Occ.	U_{iso} (Å^2)
Bi	4e	0.0	0.0	0.16841(5)	1.0	0.0544(6)
M (V/Ge)	2b	0.5	0.5	0.0	0.65/0.35	0.064(1)
O(1)	4d	0.0	0.5	0.25	1.0	0.0391(5)
O(2)	4e	0.5	0.5	0.1028(3)	0.410(5)	0.059(1)
O(3)	32e	0.575(2)	0.068(2)	0.0284(2)	0.083	0.084(3)
O(4)	16n	0.5	0.288(1)	0.0907(3)	0.147(1)	0.059(1)

Table S5. Significant contact distances in BIGEVOX35

Temp.	Bond	Distance (Å)	Bond	Distance (Å)
25 °C	Bi-O(1)	2.3326(6)	V/Ge-O(2)	1.571(6)
	Bi-O(4)	2.557(4)	V/Ge-O(3)	1.746(5)
			V/Ge-O(3′)	2.343(5)
			V/Ge-O(4)	1.622(5)
700 °C	Bi-O(1)	2.3552(7)	V/Ge-O(2)	1.596(4)
	Bi-O(4)	2.590(4)	V/Ge-O(3)	2.318(8)
			V/Ge-O(3′)	1.798(7)
			V/Ge-O(4)	1.640(6)

Table S6. Calculated V-O bond distances from Raman spectrum of BIGEVOX35.

BIGEVOX35	v (cm^{-1})	Area (%)	r (Å)
	301.0	18.40	2.22
	361.0	10.90	2.13
	424.0	4.84	2.04
	504.0	2.00	1.95
	613.0	0.32	1.85
	659.0	2.85	1.81
	717.0	6.76	1.77
	768.0	5.64	1.73
	819.0	25.28	1.70
	859.0	23.01	1.68
Average			1.87

Note: v is the wavenumber, r is the calculated bond length and s is the corresponding bond valence.