Electronic Supplementary Information for Dalton Transactions

Apatite germanates doped with tungsten: synthesis, structure, and conductivity

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Supplementary information

Figure S-1a Representative Impedance plot for $La_{10}Ge_{5.5}W_{0.5}O_{27.5}$

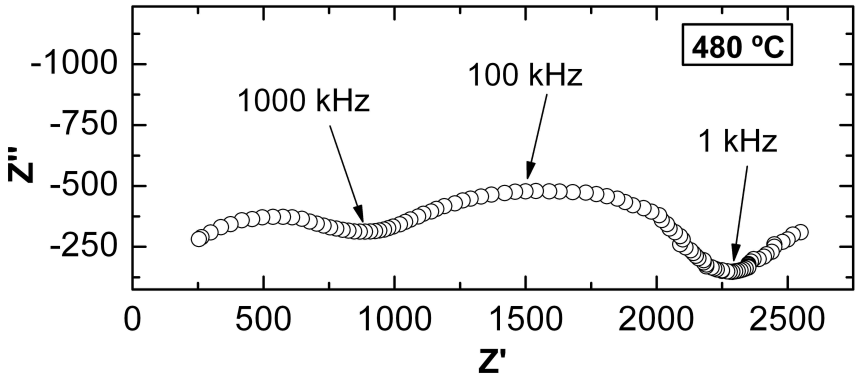

Fig S-1b SEM image for the $La_{10}Ge_{5.5}W_{0.5}O_{27.5}$ pellet (Jeol JSM-6060 LV, 20kV) (x1000)

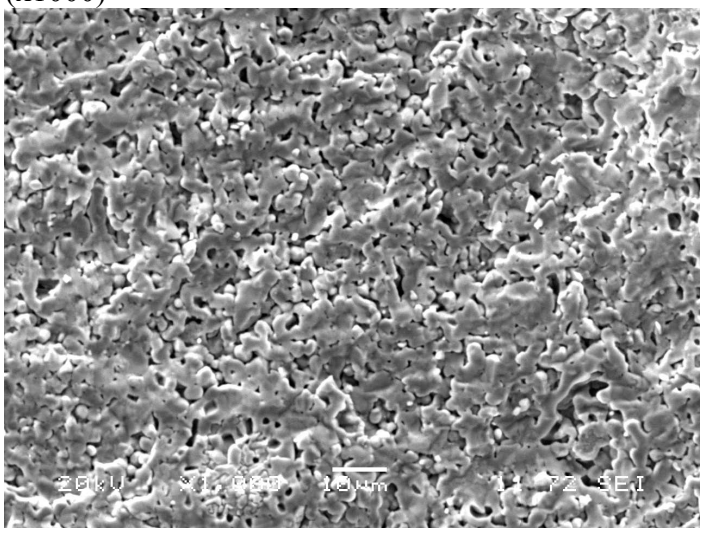

Figure S-2. Raman data line-shape analysis. The figure shows the fits of the RT and 700 °C spectra (not in the same scale) for $La_{10}Ge_{5.5}W_{0.5}O_{27.5}$ as a superposition of bands. Crosses are experimental points (only one half are shown) and the thick red line is the global fit, which includes, together with bands labelled in the figure as D, G, and W, a background and some more bands at lower wavenumbers (not shown). The integrated intensities of bands D (associated with interstitial oxygen close to GeO_4), G (which includes several bands to account for split internal modes ν_1 and ν_3 of the GeO_4 tetrahedra) and W (attributed to WO_5 entities), in arbitrary units, are given in the inset, together with the ratio of the W to the G bands. This figure shows that, despite broadening and softening effects induced by heating, the ratio W/G remains constant, within fit error. In contrast, band D disappears somewhere between 500 and 600 °C.

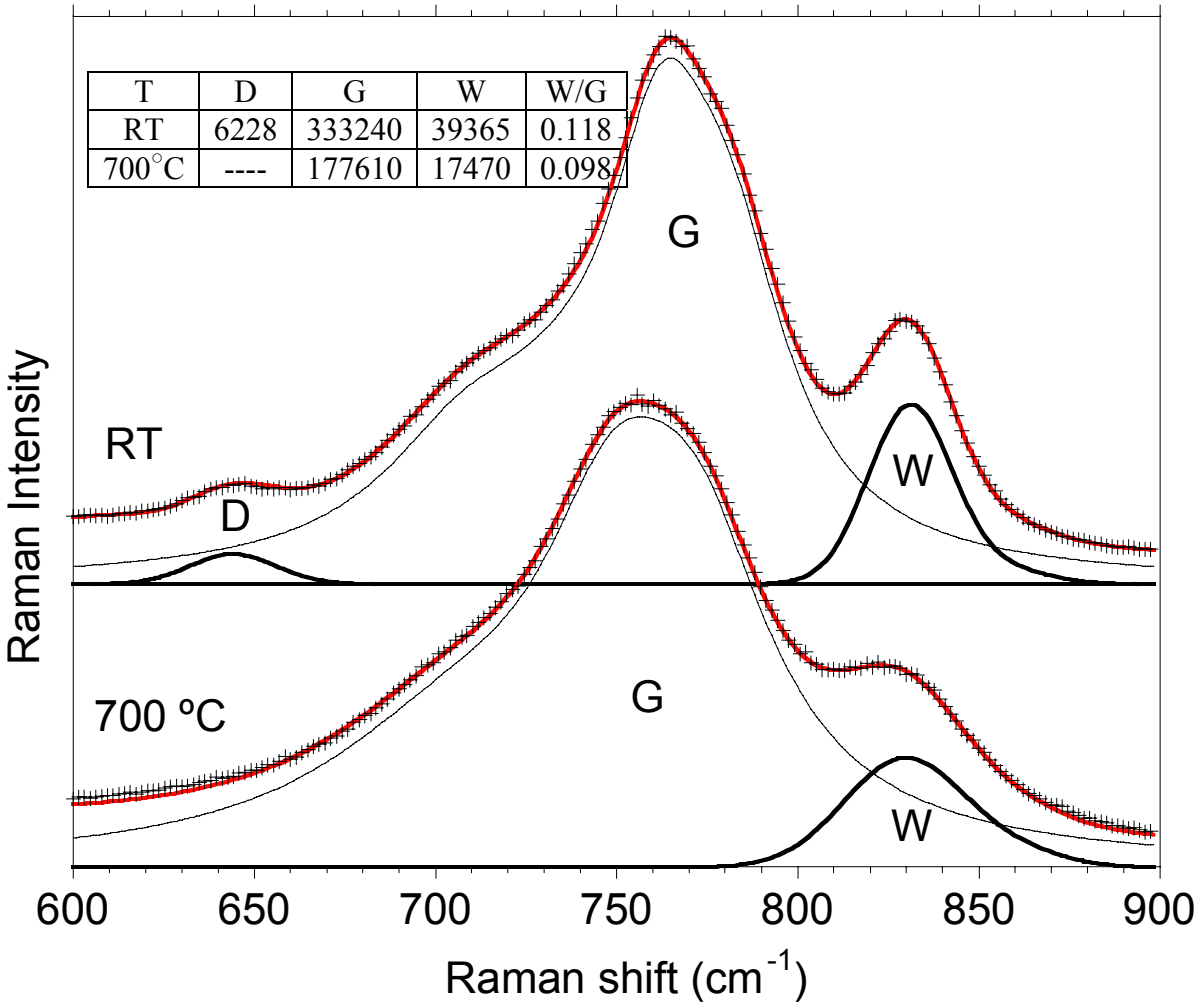

Figure S-4a: $La_{10}Ge_{5.5}W_{0.5}O_{27.5}$: Fourier map showing that the O3 site is split

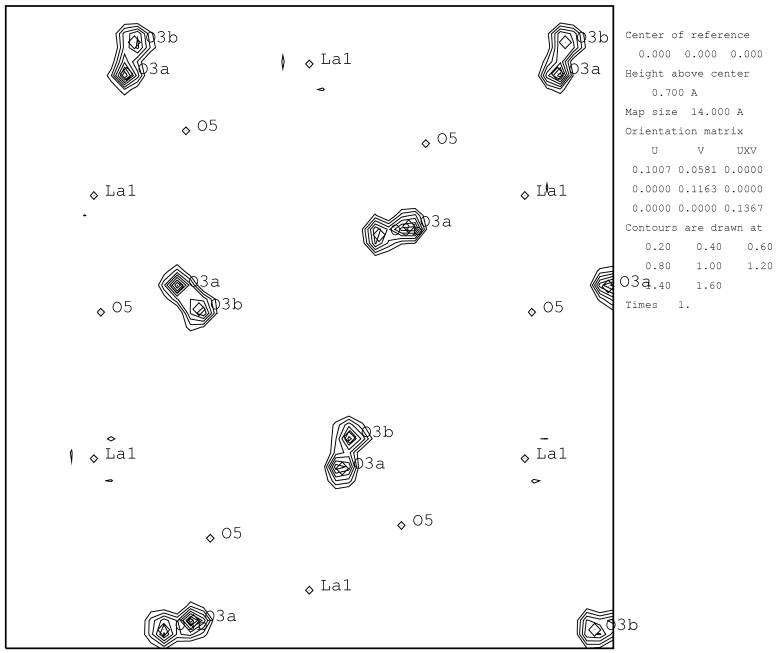

Figure S-4b $La_{10}Ge_{5.5}W_{0.5}O_{27.5}$: Fourier map showing the presence of interstitial oxide ions (O5) in the vicinity of the Ge/WO_4 tetrahedra

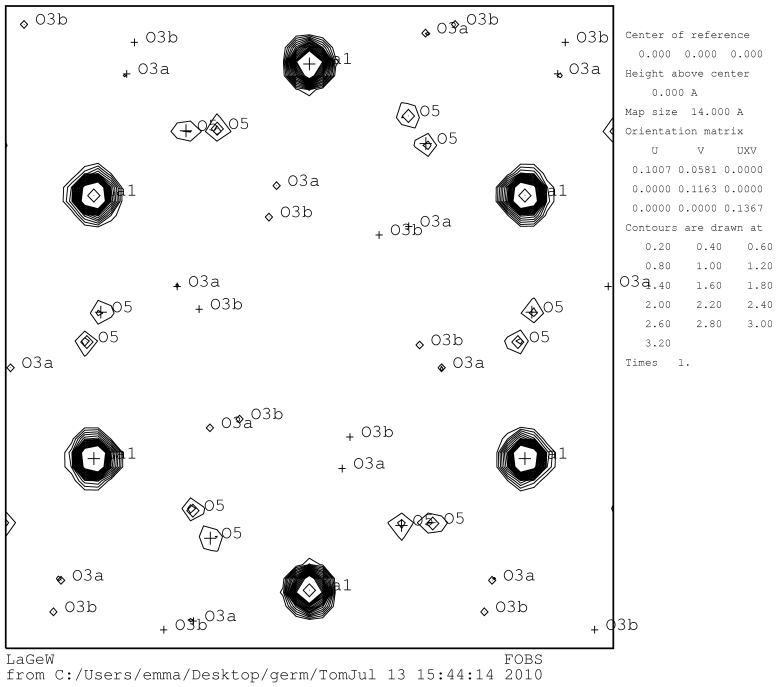

Figure S-5a Observed, calculated and difference neutron diffraction profiles for $La_{10}Ge_{5.5}W_{0.5}O_{27.5}$

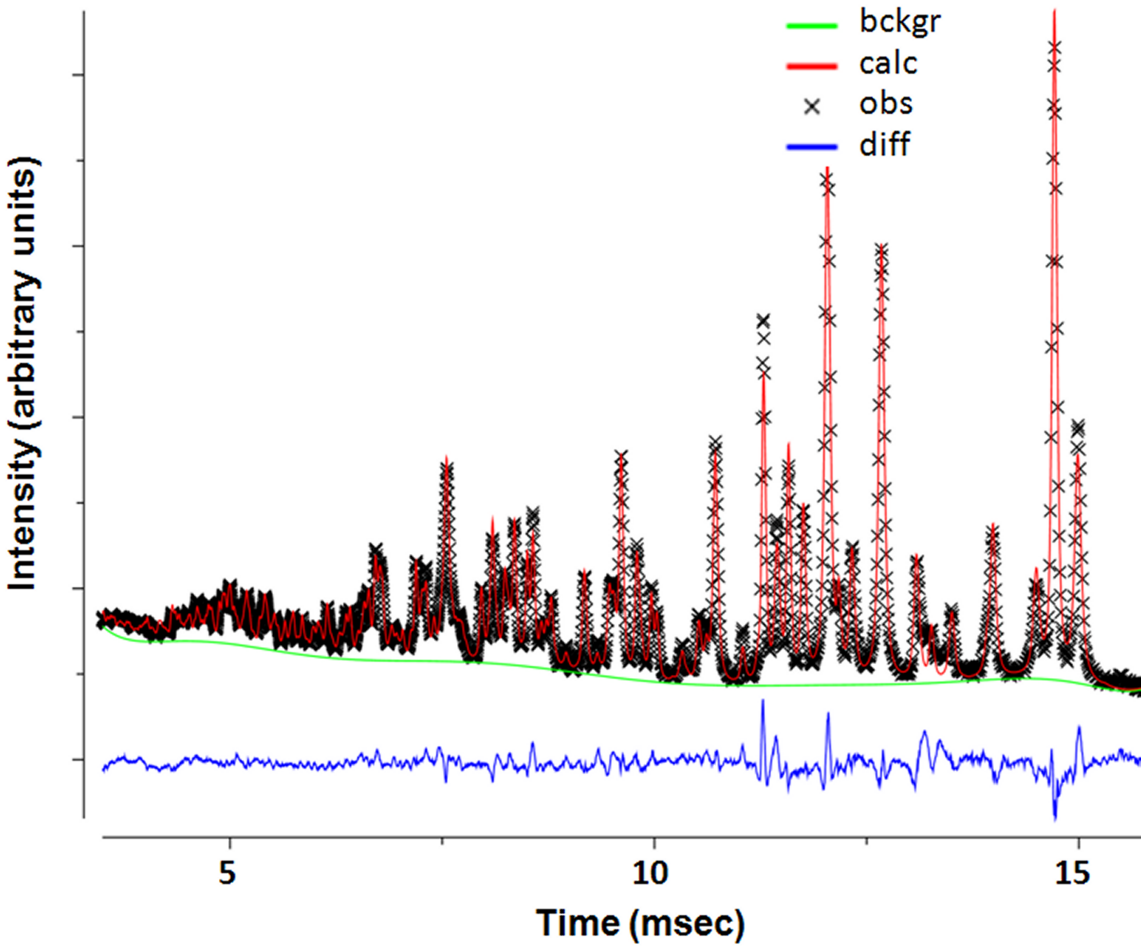

Figure S-5b Structure of $La_{10}Ge_{5.5}W_{0.5}O_{27.5}$ (tetrahedral= Ge/WO_4; trigonal metaprisms = LaO_6; yellow spheres= La, red spheres= O4 (channel oxide ions), green spheres=O5 (interstitial oxide ions)

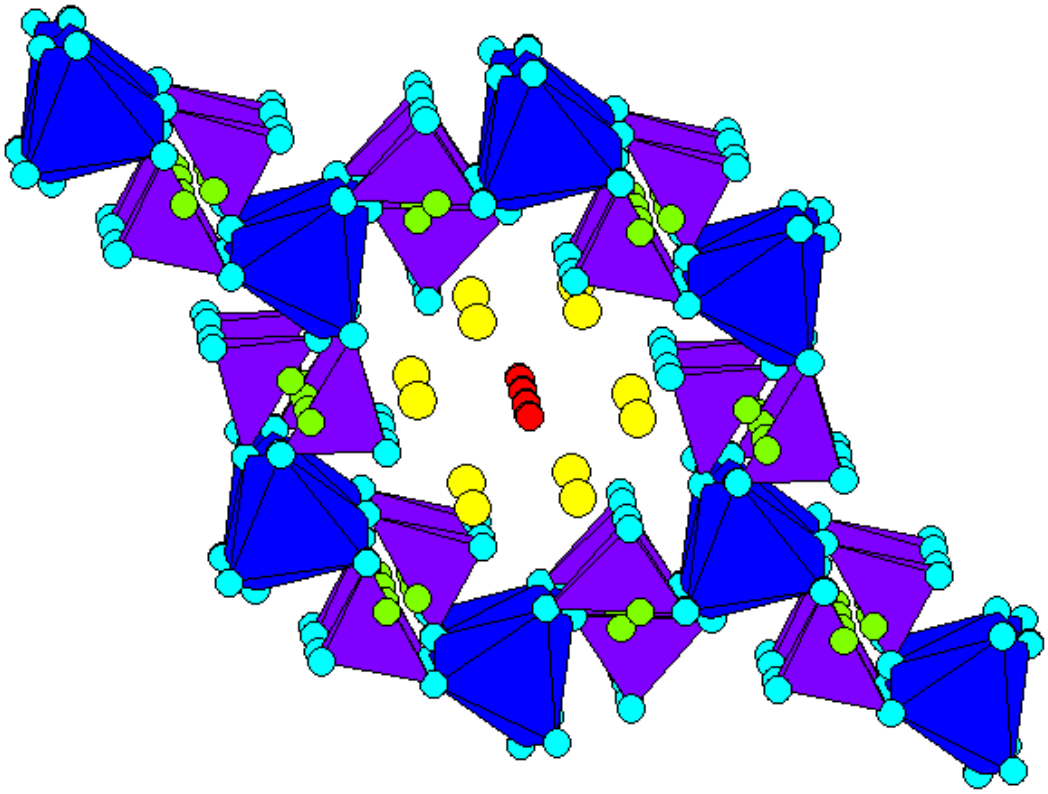

Table S-1. Refined structural model for $La_{10}Ge_{5.5}W_{0.5}O_{27.5}$ with anisotropic atomic displacement parameters rather than split sites.

S.G.	$P6_3/m$	a = 9.9302(2) Å	c = 7.3159(2) Å	R_P = 0.0378
		wR_{exp} = 0.0079	wR_p = 0.0268	R_F = 0.070
Site	***x***	***y***	***z***	**Occ.**
La(1)	1/3	2/3	0.0032(4)	1
La(2)	0.2310(2)	-0.0084(2)	1/4	1
Ge/W	0.4012(2)	0.3771(2)	1/4	0.9167/0.0833
O(1)	0.3089(4)	0.4875(3)	1/4	1
O(2)	0.6036(3)	0.4728(3)	1/4	1
O(3)	0.3385(4)	0.2508(3)	0.0696(3)	1
O(4)	0	0	1/4	1
O(5)*	0.029(1)	0.479(2)	0.508(2)	0.125

* O(5) isotropic ADP = 0.034(2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
La(1)	0.0441(9)	0.0441(9)	-0.0012(7)	0.0220(5)	0	0
La(2)	0.0101(8)	0.0057(7)	0.0152(6)	0.0006(6)	0	0
Ge/W	0.0144(8)	0.0045(7)	0.0111(7)	0.0049(7)	0	0
O(1)	0.056(2)	0.018(2)	0.030(2)	0.030(2)	0	0
O(2)	0.023(2)	-0.0099(9)	0.067(2)	-0.0060(9)	0	0
O(3)	0.187(3)	0.033(1)	0.0123(8)	0.055(2)	-0.055(1)	-0.0143(9)
O(4)	0.028(2)	0.028(2)	0.182(8)	0.0049(7)	0	0

Bond	**Distance (Å)**
O(5) – O(1)	2.599(13), 2.660(13)
O(5) – O(2)	2.106(15), 2.335(14)
O(5) – O(3)	1.817(15), 2.655(13)