Profile refinement strategy

Various data analysis strategies were applied. Initial fitting of a single 30 minute data set showed excellent statistics in the data collection and the extracted crystallographic parameters. The handling of errors within Rietveld programs has been discussed in detail.[14] In terms of the derived esds on extracted crystallographic parameters no improvement in the values could be obtained by summing data sets and thus all further refinements were undertaken on the individual 30 minute sets. Full profile fitting, between 10 and 150 °, was achieved by variation of all key profile and crystallographic parameters. The former included variation of lattice parameter, peak shape parameters (U, V, W, LX, LY and asymmetry), background coefficients (4 term polynomial), scale factor. Variation in zero point and/or sample displacement was also studied to investigate for any significance or effects as a result of sample remounting or instrument changes; no effect was observed with the zero point varying by less than 0.001° and sample displacement invariant – hence these values were maintained at the values extracted from the calibration run. All data sets were thereafter dealt with in an identical fashion in terms of the parameters refined. Crystallographic parameters varied were all atomic positions, isotropic thermal displacement parameters (TDPs) for atoms on high symmetry sites (Cl(Br), Al, Si) and anisotropic TDPs for sodium and oxygen. Investigation of the site occupancy factors for halide showed that a small deficiency on this site could be determined (refining typically to 0.980(2)) representing the vacancies and partial occupation of this site by sulphur. In order to ensure consistency in the refinements this site occupancy factor was fixed at 0.98. All refinements converged rapidly to give excellent fits to the data and extracted profile and positional parameters with very low esds.

Table S1. Crystallographic model used to fit all profiles. Extracted data as obtained from the GSAS output from an example data set, a coloured chloride sodalite.

Atom	Wyckoff letter. Site symmetry	x	y	z	U_{iso}/U_{eq}(*) / x 100 (Å^2)	Occupancy
Na1	8e . 3 .	0.17807(4)	0.17807(4)	0.17807(4)	1.97*	1
Cl2	2a 2 3 .	0	0	0	2.73(4)	0.980
Si3	6c -4 . .	0.0	0.25	0.5	0.66(6)	1
Al4	6d -4 . .	0.25	0	0.5	0.41(6)	1
O5	24i 1	0.14204(4)	0.14916(4)	0.43864(3)	1.14*	1

Atom	U_{11} x 100 (Å^2)	U_{22} x 100 (Å^2)	U_{33} x 100 (Å^2)	U_{12} x 100 (Å^2)	U_{13} x 100 (Å^2)	U_{23} x 100 (Å^2)
Na1	1.97(5)	1.97(5)	1.97(5)	0.14(5)	0.14(5)	0.14(5)
O5	0.91(7)	1.41(7)	1.11(2)	0.51(3)	0.35(5)	-0.14(5)

Space Group P -4 3 n, a = 8.88461(5) Å, wR_p = 3.60 % R_p = 2.36 % R_I = 2.01%

Table S2. Key extracted bond distances (Å) and angle(°) for the crystallographic model of Table 1. Esds in parentheses

Na1-Cl2	Na1-O5	Na1-O5’	Si3-O5	Al4-O5	Si3-O5-Al4
2.7403(8)	2.3533(4)	3.0803(3)	1.6286(3)	1.7334(3)	138.22(5)

CIF files for all refinements are available on request from the principal author.

Table S3. Comparison of extracted, mean structural parameters for white, coloured and bleached photochromic sodalites. Upper half $Na_8[AlSiO_4]_6[Cl_{2-x-y}S_x\square_y]$, lower half $Na_8[AlSiO_4]_6[Br_{2-x-y}S_x\square_y]$. Esd's from statistical analysis of all data collected from that electronic state/colour form.

Parameter Distance(Å) /Angle(°)	*White*	*Coloured*	*(Part) Bleached*
a	8.88406(6)	8.88459(3)	8.88427(9)
Na1-Cl2	2.7401(5)	2.7399(5)	2.7400(3)
Na1-O5 (x3)	2.3531(2)	2.3536(2)	2.3534(2)
Na1-O5‘ (x3)	3.0801(1)	3.0804(1)	3.0803(2)
Si3-O5	1.6287(2)	1.6287(2)	1.6285(2)
Al4-O5	1.7330(3)	1.7331(2)	1.7331(2)
Si3-O5-Al4	138.23(1)	138.23(1)	138.24(1)
a	8.93997(5)	8.94038(5)	8.94002(11)
Na1-Br2	2.8800(6)	2.8790(6)	2.8788(10)
Na1-O5 (x3)	2.3565(2)	2.3568(3)	2.3566(1)
Na1-O5’ (x3)	3.0392(2)	3.0394(2)	3.0392(2)
Si3-O5	1.6253(2)	1.6253(1)	1.6252(2)
Al4-O5	1.7357(2)	1.7359(2)	1.7358(2)
Si3-O5-Al4	140.23(1)	140.23(1)	140.23(1)

Supplementary Information Figure Captions

Figure S1. Final fit obtained to the powder neutron diffraction profile of $Na_8[AlSiO_4]_6[Cl_{2-x-y}S_x\square_y]$ – typical 30 minute run. Observed data is shown as crosses, calculated profile is the upper continuous line and the difference the lower continuous line. Reflection positions are represented by tick marks. Inset shows one region expanded.

Figure S2. Variation in the extracted Si-O distance in $Na_8[AlSiO_4]_6[Cl_{2-x-y}S_x\square_y]$ in white, coloured and bleached states. Horizontal lines show average value for that state.

Figure S1

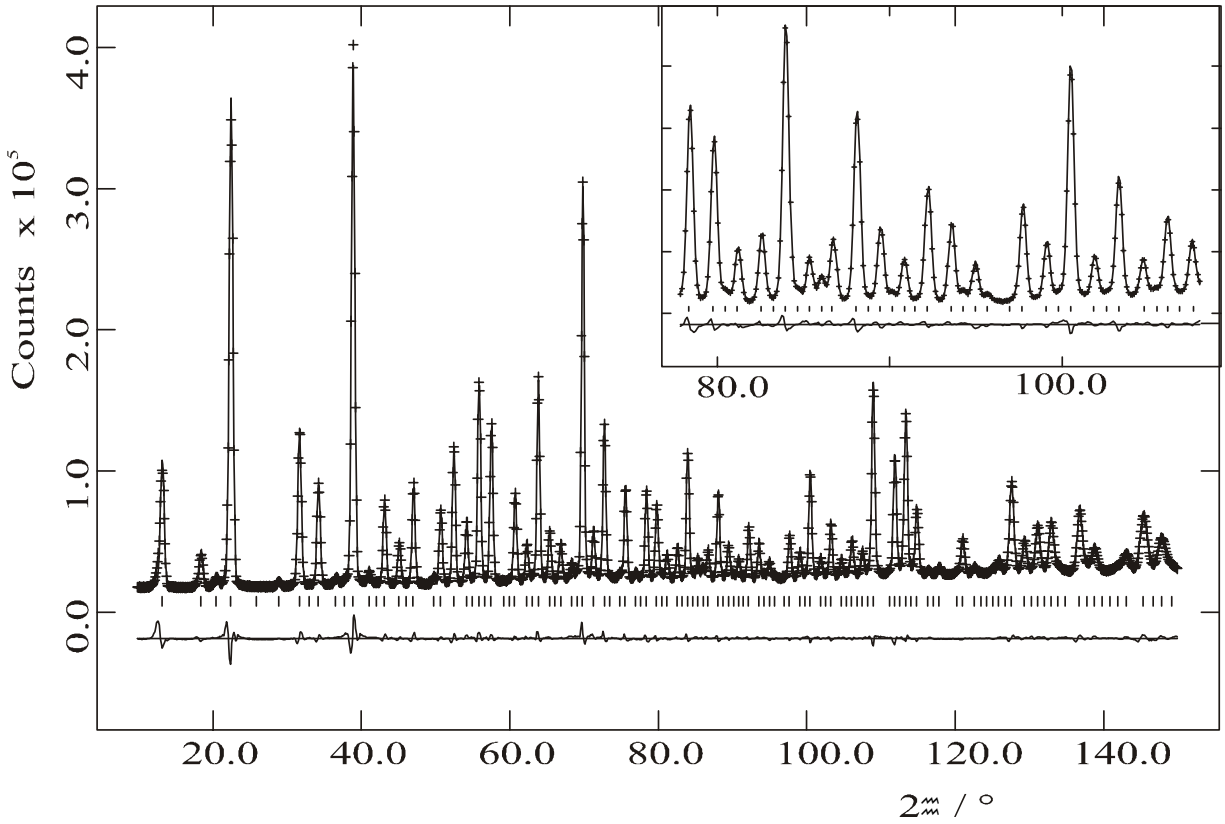

Figure S2