Structural observation of photochromism†

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The reversible formation of a long-lived, coloured F-centre has been observed in small structural changes delineated by neutron diffraction.

Materials that demonstrate reversible colour changes induced by exposure to radiation of various wavelengths, ***photochromism***, have applications that include photochromic lenses, filters, information storage, smart coatings for windows/sun-blinds, specialist clothing and jewellery. Photochromic materials sensitive to UV radiation include a number of organic compounds, such as the spiroxanes, glasses containing silver salts and some members of the sodalite family of minerals. Photochromic materials of most interest are those that colour when irradiated with UV radiation; in some systems this colour can be later bleached on exposure to ambient light, and the whole process is fully reversible. The phenomenon is exemplified in crystalline inorganic systems by the mineral hackmanite[1] and synthetic equivalents with the sodalite type structure, where a deep pink or violet colour can be induced by a short, typically of a few seconds, exposure to UV radiation, see Fig. 1; this colour fades in natural light over a period of a few minutes. Photochromic materials based on extended π-electron systems such as spiropyrans, benzochromenes and spiroxazines are well known,[2] but these molecular systems have poor long term light and heat stability, reducing potential applications. In photochromic glasses the colouring process involves the formation of silver clusters from silver salts incorporated within the glass[3] and the colouration range achievable is limited to, typically, grey and brown hues. We have determined for the first time the subtle modifications in structure that occur when a photochromic material is transformed to its brightly-coloured, F-centre containing, excited state. To do this we have used very high intensity, powder neutron diffraction, thus avoiding photo-excitation of the material, to study both coloured and bleached forms of two photochromic materials.

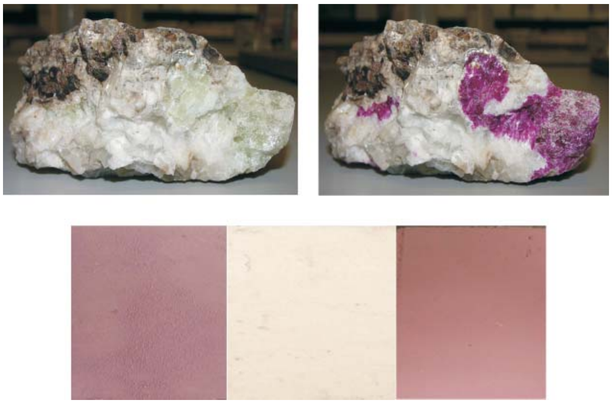

Fig. 1 Upper pictures: A mineral sample containing hackmanite (from Kangerlussaq, Ilimaussaq Complex, Greenland) before and after exposure to UV radiation (254 nm, 10 s, 3400 μW/cm^2). Lower pictures: Synthetic samples of photochromic sodalites before (centre) and after (left $Na_8[AlSiO_4]_6[Br_{2-x-y}S_x\square_y]$, right $Na_8[AlSiO_4]_6[Cl_{2-x-y}S_x\square_y]$) excitation under the same UV light.

The photochromism in sodalite structures involves the reversible formation of long-lived F-centres, Fig. 1.[4–6] The F-centre has a lifetime of minutes under ambient (daylight, room temperature) conditions and the colour persists until sufficient energy is available (often in the form of natural light or heat) to allow the electron to escape its trap; in the dark at room temperature the F-centres persist permanently. In these materials the F-centre is believed to derive from an electron that is ionised from an anionic species in one cage, probably S_2^{2-}, and trapped on a vacant anion site in a nearby cage (Fig. 2) and significant levels (a few percent of the cages) of these F-centres may be introduced by controlling the stoichiometry. The colour of the photo-excited material can be controlled producing red, violet and blue shades as determined by the size of the F-centre.[7–9] The structural changes observed following the formation of an excited state of a molecular compound have provided detailed information on the electron redistributions. These molecular modifications accompanying the formation of an electronically excited state have been revealed for a number of single crystal forms of molecular compounds using time resolved, high intensity X-ray crystallography.

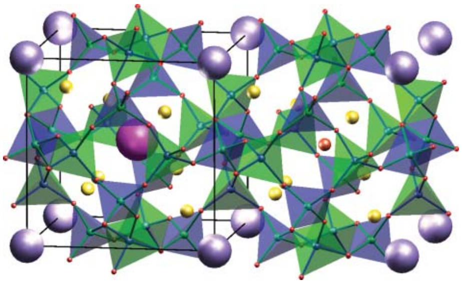

Fig. 2 The sodalite structure showing the framework as SiO_4 (green) and AlO_4 (purple) tetrahedra surrounding cages containing sodium ions (gold spheres) and anion sites (purple). Two sodalite cages are shown: the left hand one contains an ionisable anion (magenta) from which an electron is transferred to the previously vacant, neighbouring right-hand cage (small brown sphere).

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† Electronic supplementary information (ESI) available: Full crystallographic description, example profile fit, extracted structural information in graphical and tabular forms, example CIF file. See DOI: 10.1039/b517715d

Such studies are typified by the work of Coppens,[10] and Raithby and Cole[11] and are key to understanding the interaction of photons with photo-active compounds in relation to applications such as photochromism, information storage, optical computing and photosynthetic processes.

To characterise the structural changes that occur in photochromic sodalites, with lower levels colour centres, a new approach is required that allows the study of polycrystalline material, highly sensitive to X-ray radiation but with a long (potentially infinite) excited state lifetime. To address the problem we have used high intensity powder neutron diffraction to study photochromic materials in their uncoloured, coloured and bleached states; unlike X-rays thermal neutrons have insufficient energy to colour or bleach these materials. Two compounds were studied; a pure synthetic chloride sodalite doped with sulfur and a bromide analogue; materials were compositionally optimised to produce a strong colouration following exposure to UV (254 nm) radiation. Neutron diffraction data were collected on the D20 diffractometer, ILL Grenoble[12] and analysed using the GSAS structure refinement suite.[13] Various strategies were used in the data analyses to check for and eliminate any systematic errors – see Experimental.‡[14] An example set of crystallographic parameters and derived distances/angle of interest, extracted from a typical structure refinement, are summarised in the Supplementary Information (Tables S1 and S2).§ Samples were pure and no non-sodalite phase reflection was observed in the diffraction profiles even with summed data sets containing over 10^7 counts in the reflections. Profile fitting was of very high quality as represented by excellent fit factors and the final observed fit for a typical 30 minute data collection period is included in the Supplementary Information.

Key crystallographic parameters and derived bond lengths were extracted from each of the refinements and selected values are plotted in Figs. 3 and 4. The main change observed was in the lattice parameter, which increased significantly for both the chloride and bromide based forms in the coloured material containing the F-centres, Fig. 3. This change in lattice parameter is reversed on bleaching though for the chloride based sample the value does not return fully to the original distance, a behaviour probably associated with incomplete bleaching of the compound (a faint colouration remained after the 30 minute bleaching period). Note that the lattice parameter is defined precisely as a result of the large d-spacing range used and sensitivity of the complete profile to this parameter; extracted positional parameters and derived bond lengths/angles are less precisely defined (with larger esds generated within GSAS) as these values are more strongly inter-correlated and depend on changes in peak intensity rather than peak position. However, small changes for some distances can be discerned while other bond lengths are invariant on UV activation and bleaching. Thus, the framework geometry is unaffected by the photochromism while some very small changes are discernible for the non-framework ion positions and derived bond distances, Fig. 4. These changes are of a similar magnitude to the extracted esds from the GSAS program but it should be noted that the actual variation within the sets of derived distances is experimentally much lower, about a factor of 2–3, and thus the differences are of greater significance. In order to compare the white, coloured and bleached samples mean values and associated statistical esds were obtained for each compound in the excited/non-excited state. Values are summarised in Supplementary Information, Table S3. Changes in most of the derived bond angles and distances were within the esds but some extracted bond lengths show significant changes between the white and coloured materials. It is notable that despite the increase in lattice parameter the Si–O and Al–O distances and the Si–O–Al angle are all unaffected within 0.0002 Å/0.01°; this consistency confirms the accuracy of the values extracted.

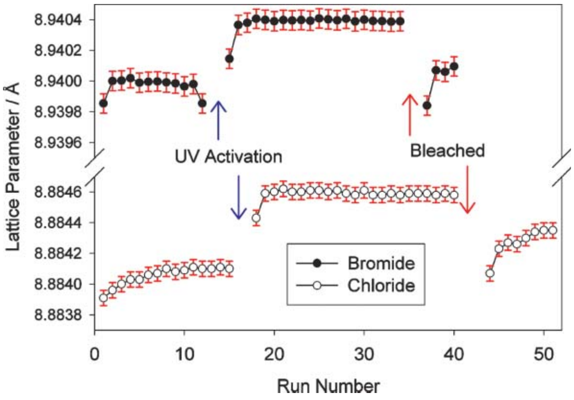

Fig. 3 Variation of the lattice parameters of $Na_8[AlSiO_4]_6[Cl_{2-x-y}S_x\square_y]$ and $Na_8[AlSiO_4]_6[Br_{2-x-y}S_x\square_y]$ as determined from the Rietveld profile refinements in white, coloured and bleached states.

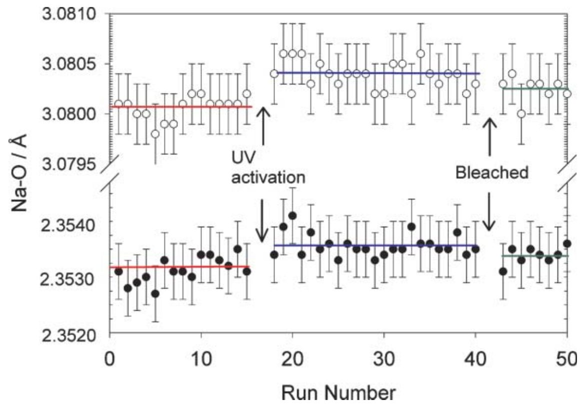

Fig. 4 Variation in the extracted Na–O distances in $Na_8[AlSiO_4]_6[Cl_{2-x-y}S_x\square_y]$ in white, coloured and bleached states. Horizontal lines show average value for a state. Error bars from GSAS.

Considering the sulfur-doped chloride sodalite, first there is an observed small increase in the Na–O distances (Fig. 4) and a negligible or, possibly very small, decrease in the Na–Cl distance. This behaviour can be rationalised in terms of the colouring process where an electron is believed to be transferred from an S_2^{2-} unit in one cage to a vacant site (□) in another,[15] thus: $[S_2^{2-}] + \square \rightarrow [S_2^{-}] + [e^{-}]$

The overall effect of this transfer on the structure is most apparent in the reaction of the sodium ions adjacent to these active sites. Note that as the vast majority of the sodium ions are in cages that contain chloride ions, and are unperturbed by this electron transfer, any measured changes in atomic positions will be strongly diluted by scattering from unmodified cages. The level of F-centres in these materials has been measured at around 0.1–2%.[15] Despite this small concentration, the formation of the F-centre is observable as a small expansion in the sodium to oxygen atom distances and the lattice parameter while maintaining the sodium to cage centre distance. These changes sum together to produce the overall expansion in lattice parameter observed. A possible

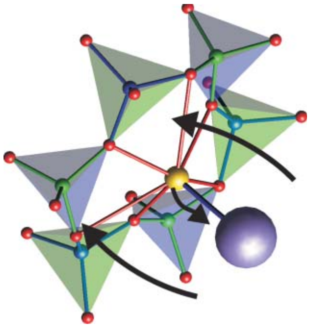

Fig. 5 The sodium (gold sphere) environment in sodalite showing the six-membered ring formed from AlO_4 and SiO_4 tetrahedra and coordination to the central anion (purple sphere). The arrows show the structural changes that occur following photo-excitation.

interpretation of this observed positional shift is that there is a stronger electrostatic interaction between sodium and the $[S_2^- + e^-]$ cage filling arrangement (than with $[S_2^{2-} + \square]$) and this pulls the sodium away from the framework. This happens while maintaining, rather than decreasing, the effective size of the anionic/neutral species at the cage centre. This shift in the excited state leads to the overall expansion of the structure as the Na–O distances lengthen due to a weaker O–Na interaction as illustrated in Fig. 5. A further valid comparison can be made with the structure determinations of stoichiometric sodalites $Na_8[AlSiO_4]_6Cl_2$ obtained using the same powder neutron diffraction technique or X-ray diffraction.[16] A natural photochromic sodalite has also been investigated.[17] In the absence of any sulfur/vacancy on the anion site the observed lattice parameter and sodium co-ordination distances are distinctly smaller (*e.g.* the lattice parameter of synthetic sodalite is 8.8812 Å[16]) compared with doped, sulfur containing sodalites. The same is true of naturally occurring materials, for example, hackmanite has a lattice parameter of 8.877 Å[17] compared with natural sodalite 8.870–8.873 Å.[18] Thus, incorporation of the sulfur/vacancy pair into the sodalite cage causes a small expansion of the structure and all the Na–(O,Cl,(S),□) distances. Photo-excitation causes further overall expansion but the sodium ion shifts position to coordinate more strongly to the trapped electron.

For the sulfur-doped bromide sodalite the overall structural changes are weaker as seen by a relatively smaller increase in lattice parameter and associated weaker trends in extracted bond lengths. Again there is evidence, albeit weak, for a movement of sodium away from the framework towards the cage centre on colouration with a significant decrease in the sodium to cage centre distance. The less prominent effect in this phase is probably associated with the fact that the framework is already more expanded to accommodate the larger bromide ion and the formation of the colour centre perturbs the structure less strongly.

These results provide the first direct observation of the structural changes that occur in a solid following formation of F-centres. This extracted crystallographic information allows a model of the excited state to be constructed which will in turn lead to a better understanding of the excitation processes in these and other important materials.

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Notes and references

‡ **Experimental** Samples of synthetic hackmanite of the nominal composition ($Na_8[AlSiO_4]_6[Cl_{1.6}S_{0.1}\square_{0.1}]$ where □ represents a vacancy) were prepared using solid state methods. Zeolite A (dried at 500 °C), NaCl (or NaBr) and Na_2SO_4 in the ratio, by weight, of 70%, 24% and 6%, respectively, were ground together and then annealed in air at 850 °C for 48 hours. The samples were removed, re-ground and then annealed for 2 hours at 850 °C under a reducing atmosphere of 5% hydrogen, 95% nitrogen. This annealing treatment activates the samples, reducing sulfate to S_2^{2-} so they become UV responsive. Products were washed with warm distilled water to remove all excess of NaCl/NaBr and dried at 110 °C. Powder X-ray diffraction patterns collected on a Siemens D5000 confirmed phase purity. Chemical analysis using XRF showed Cl and S levels in the chlorosulfo-sodalite consistent with the composition $Na_8[AlSiO_4]_6[Cl_{1.85\pm0.1}S_{0.1\pm0.02}]$; the reduced (compared with the reaction stoichiometry) sulfur content is consistent with previous analyses[9,15] and reflects some loss during the reaction. ESR spectra of white and UV activated samples were in agreement with literature data,[15] confirming the presence of significant levels of S_2^{2-}/S_2^-.

Powder neutron diffraction data were collected on the D20 diffractometer at the ILL, Grenoble operating in high resolution/high angle take off mode. Data were collected using a previously calibrated wavelength of 1.374 Å, which represented an optimised intensity and resolution for this system. For each Cl/Br based material data were collected from a single sample, initially in the unactivated white state, then the same sample coloured through prolonged exposure to UV light and, finally, this identical sample bleached (de-coloured by exposure to a normal tungsten filament lamp). 5 g of sample was mounted in a 12 mm diameter vanadium sample can and data sets were collected in 30 minute blocks; for each sample, in each state of activation, between 5 and 20 separate data sets were collected. In order to check for, and eliminate, systematic errors resulting from sample mounting, the sample can was periodically removed from and then remounted on the instrument. Samples were activated by grinding for 30 minutes under a 3400 μW/cm^2 UV lamp producing 254 nm radiation; intensely coloured materials were obtained with high levels of F-centres.[15] Samples were deactivated by grinding for 30 minutes under a 60 Watt tungsten lamp though in the case of the chloride based sample incomplete bleaching was achieved under these conditions and the sample remained slightly coloured. The sample volume within the beam was identical for each sample type. The temperature of the sample environment was monitored but did not vary significantly over the total experiment period of 48 hours. Various data analysis strategies were applied as detailed in the supplementary information. All refinements converged rapidly to give excellent fits to the profile and positional parameters with very low esds.

§ CCDC 293403. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517715d

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