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Heteroanionic intercalation into positively charged inorganic hosts: the first nitride mixed halides†

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The first nitride mixed halides have been synthesised by disordered intercalation of anions between the positively charged layers of subnitride hosts.

Intercalation reactions are used extensively in solid state chemistry not only to access new compounds or polymorphs, but also in the synthesis of a wide range of commercially important materials such as zeolites and layered transition metal oxides and sulfides. The dominating pattern in this area of chemistry is the insertion of cationic guests into neutral or ostensibly negatively charged 2D or 3D hosts. The ability to intercalate negatively charged species is restricted to a relatively small and exclusive group of host materials, of which graphite and its intercalation compounds (GICs) are well-known examples. In fact, graphite is exceptional in its capacity to act as both electron acceptor (*e.g.* C_8K) and electron donor (*e.g.* C_8Br).[1] Furthermore, the hydrotalcite group of clays are unusual examples of 2D hosts containing formally positively charged layers.[1,2]

Intercalation in nitride chemistry is relatively undeveloped and is largely limited to the insertion of lithium and other alkali metals. Most notable has been the intercalation of Li^+ into Zr(Hf)NCl to induce superconductivity at *ca* 25 K,[3] although other isolated examples exist (*e.g.* 3D insertion in the $Na_xTa_3N_5$ system).[4] One interesting aspect of nitride chemistry, however, is the propensity for compounds to form *anti*-structures; frameworks that are the antithesis of some of the most common 'normal' structures seen in oxide chemistry (*e.g. anti*-perovskites, M_3NX; *anti*-fluorites $(Li,M)_2N$ *etc.*).[5] These *anti*-structures can be exploited for new synthetic and materials chemistry. Here we report our initial investigations of mixed *anion* intercalation in subnitride hosts with layered *anti*-$CdCl_2$ structures to produce the first examples of nitride mixed halides.

Nitride halides $A_2N(X,X')$ (A = Ca, Sr; X, X′ = Cl, Br, I) were synthesised by reaction of the binary alkaline earth nitrides (Ca_3N_2, Ca_2N or Sr_2N), AX_2 and AX'_2 at elevated temperatures (typically 800–1200 °C) under anaerobic conditions. Binary nitrides were prepared first by reaction of the alkaline earth metals under nitrogen in liquid sodium solvent as described previously.[6,7] We also observed that A_2NX species spontaneously form at lower temperatures by reaction of the subnitride with halogen (*e.g.* shaking together Sr_2N and I_2) or an anhydrous transition metal halide salt (*e.g.* grinding Ca_2N and $FeCl_3$ in a mortar in an Ar-filled glove box). Both these processes begin at room temperature and are highly exothermic. The former process leads to a crystalline powder with a powder X-ray diffraction (PXD) pattern that cannot yet be indexed, the latter to microcrystalline Ca_2NCl and iron powder.

Nitride halides were initially characterised by PXD using a Philips Xpert diffractometer with Cu-Kα radiation.‡ Analysis and subsequent indexing of powder data revealed continuous solid solutions existing in the A_2N(Cl, Br) systems (A = Ca, Sr). The hexagonal *anti*-α-$NaFeO_2$ structure (filled *anti*-$CdCl_2$ structure) is retained across the entire solubility range ($A_2NCl_{1-y}Br_y$; $0 \leqslant y \leqslant 1$) with no evidence of superstructure reflections (Table 1). We see no evidence of staging or ordering in these $A_2N(X,X')$ compounds and Cl and Br statistically occupy the 3a (0,0,0) site within the van der Waals type gap of the subnitrides.

Preliminary Rietveld refinement of PXD data collected for $Sr_2NCl_{1-y}Br_y$ (y = 0, 0.33, 1) compounds using the GSAS package[7] confirms that the nitride halides crystallise in space group $R\bar{3}m$ with the *anti*-α-$NaFeO_2$ structure with Cl^- and Br^- disordered on the 3a site between $[Sr_2N]^+$ layers in the y = 0.33 compound. The Sr–N 2D ionic framework does not change dramatically as a function of intercalant concentration. Sr–N bond length increases slightly [2.618(1) to 2.626(1) Å] and $[Sr_2N]^+$ layer thickness decreases (*via* angular compression of NSr_6 octahedra) from 2.68 Å in Sr_2NCl (R_{wp} = 11.51%, R_p = 8.26%, χ^2 = 2.91) to 2.63 Å in Sr_2NBr (R_{wp} = 11.29%, R_p = 8.04%, χ^2 = 2.81). The ionic layers thus separate to accommodate the larger anion and the interlayer gap increases (from 4.31 Å in Sr_2NCl to 4.65 Å in Sr_2NBr).

A detailed structural description of the Ca_2N(Cl,Br) system was obtained by GSAS[8] refinement of time of flight (ToF) powder neutron diffraction (PND) data collected using the high intensity diffractometer POLARIS at ISIS, Rutherford Appleton Laboratory. Diffraction data were collected for $Ca_2NCl_{1-y}Br_y$ (y = 0, 0.6, 1) at 298 K and additionally at 150 and 75 K for $Ca_2NCl_{0.6}Br_{0.4}$. Full details of the refinements of these and other related compounds will be presented elsewhere. A profile plot for $Ca_2NCl_{0.6}Br_{0.4}$ data collected at 75 K is shown in Fig. 1. Ca_2NCl and Ca_2NBr crystallise with the *anti*-α-$NaFeO_2$ structure as previously reported in a single crystal X-ray diffraction study.[9] $Ca_2NCl_{0.6}Br_{0.4}$ (Fig. 2) also adopts this structure, with Cl^- and Br^- disordered on the 3a site at 298 K and there is no evidence for a phase transition to an ordered halide anion arrangement at lower temperature. The structure is one of $[Ca_2N]^+$ layers of edge sharing NCa_6 octahedra lying parallel to the *ab* plane stacked along the *z*-direction between which are inserted halide anions $(Cl,Br)^-$. This thus creates

Table 1 Lattice parameters of $A_2N(X,X')$ nitride halides from PXD data

Compound[a]	*a*/Å	*c*/Å	*V*/Å^3	*c*/*a*
Ca_2NCl	3.6678(1)	19.718(2)	229.7(1)	5.38
$Ca_2NCl_{0.833}Br_{0.167}$	3.6732(7)	19.843(4)	231.8(2)	5.40
$Ca_2NCl_{0.667}Br_{0.333}$	3.6800(3)	19.973(2)	234.2(1)	5.43
$Ca_2NCl_{0.5}Br_{0.5}$	3.6937(3)	20.179(1)	238.4(1)	5.46
$Ca_2NCl_{0.333}Br_{0.667}$	3.699(1)	20.199(8)	239.3(3)	5.46
$Ca_2NCl_{0.167}Br_{0.833}$	3.7096(8)	20.401(6)	243.1(2)	5.50
Ca_2NBr	3.7171(4)	20.547(3)	245.9(1)	5.53
$Ca_2NBr_{0.5}I_{0.5}$	3.752(1)	21.113(5)	257.4(2)	5.63
Sr_2NCl	3.8944(2)	20.991(1)	275.7(1)	5.39
$Sr_2NCl_{0.67}Br_{0.33}$	3.9052(2)	21.232(2)	280.4(1)	5.44
$Sr_2NCl_{0.5}Br_{0.5}$	3.916(1)	21.490(9)	285.4(3)	5.49
Sr_2NBr	3.9341(3)	21.853(2)	292.9(1)	5.55

[a] Nominal stoichiometry.

† Electronic supplementary information (ESI) available: OCD profile plots for data from each POLARIS detector bank. See http://www.rsc.org/suppdata/cc/b1/b105448c/

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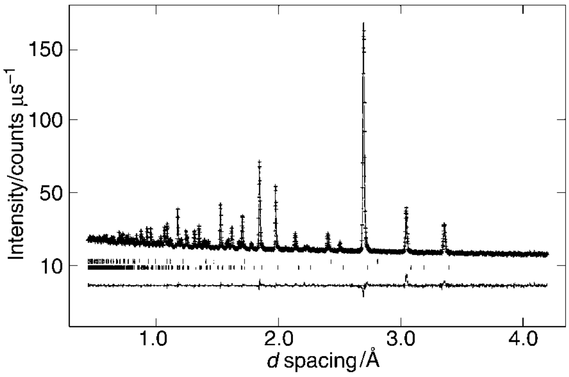

Fig. 1 Observed (crosses), calculated (solid line) and difference (below) profile plot for $Ca_2NCl_{0.6}Br_{0.4}$ PND data collected from the 90° detector bank at 75 K. Tick marks denote the major phase and CaO impurity.

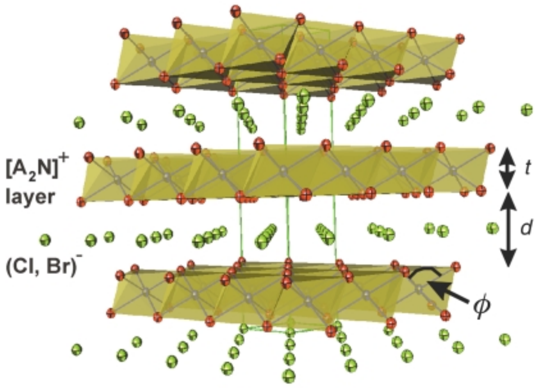

Fig. 2 Structure of $Ca_2N(X,X')$ indicating layer thickness (*t*), interplanar distance (*d*) and Ca–N–Ca angle, *ϕ*.

alternating edge sharing layers of NCa_6 and $(Cl,Br)Ca_6$ octahedra.

The Ca–N bond lengths in the $Ca_2NCl_{1-y}Br_y$ nitride halides are typical of the distances found in Ca containing nitrides. These are 2.4462(2), 2.4574(2) and 2.4679(2) Å for $y = 0, 0.6$ and 1 respectively, compared to 2.46 Å in α-Ca_3N_2 and 2.4426(4) Å in the subnitride host itself, Ca_2N.[7,10] As in the $Sr_2N(X,X')$ compounds, the $[Ca_2N]^+$ framework is fairly robust. As the average size of the anionic intercalant increases, so the $[Ca_2N]^+$ layer compresses along *z* through angular distortion of the N–Ca octahedra. The Ca–N–Ca angle, ϕ (see Fig. 2) increases from 97.09(1)° in Ca_2NCl to 97.77(1)° in Ca_2NBr. As a result the intralayer Ca–Ca distances increase [to 3.7187(1) Å along layers and 3.246(1) Å across layers in Ca_2NBr] but remain shorter than that in Ca metal (3.94 Å).[11] In turn the layers separate to accommodate the larger halide and Ca–X distances increase; $y = 0$: 2.9542(3) Å, $y = 0.4$: 3.0226(2) Å, $y = 1$: 3.0818(2) Å. The ratio of layer thickness, *t*, to interlayer distance, *d* thus changes from 0.65 in Ca_2N[7] through 0.59 (Ca_2NCl) and 0.57 ($Ca_2NCl_{0.6}Br_{0.4}$) to 0.55 in Ca_2NBr.

Whereas mixed halide compounds themselves are quite prevalent [*e.g.* $Sr(Br,I)_2$, $InBrI_2$ *etc.*][12] and disorder of multiple halides is seen in oxyhalides [*e.g.* $BaCuO_2(Br,I)$, $WOCl_3Br$],[13] these compounds are the first examples of nitride mixed halides. The $A_2N(X,X')$ nitrides are also, more generally, the first examples of heteroanionic intercalation of any sort in A_2N subnitride hosts. The $[A_2N]^+\cdot(e^-)$ formulation describing ionic layers constraining free electrons within van der Waals gaps suggests a highly reactive environment for intercalation. The potential electron donor properties of these hosts are obvious and the ready incorporation of halides at room temperature is testament to the stability of the filled structures (both relative to the hosts and to AX_2). Interestingly, despite the rigidity of the A–N framework with respect to Cl, Br and I intercalation and in contrast to many examples of cation substitution in normal structured 2D chalcogenides, reaction with smaller spherical anions (*e.g.* H^-) or non-spherical species (*e.g.* CN_2^{2-}) can lead to a collapse of A–N layers and formation of 3D structures.[14] This is in contrast however to incorporation of gold (Ca_2NAu) or diazenide (SrN) where more subtle modifications of the A_2N framework allow retention of 2D structure.[15,16]

The electronic properties of the A_2N subnitrides and their intercalates are by no means well elucidated, although the expectation is that the subnitrides are 2D metals which become more insulating (less conducting) with increased intercalation of X^- (X=H, halide). Preliminary magnetic measurements were performed on powders of Ca_2N, Ca_2NCl and Ca_2NBr using a Cryogenic S100 SQUID magnetometer in the range 4–298 K. Data show weak temperature independent paramagnetism, indicating apparently little difference in magnetic behaviour between intercalated compounds and their Pauli paramagnetic hosts. More comprehensive studies of the (de)intercalation chemistry, crystal structures, magnetic and transport properties of these and other A_2N derived nitrides will be published elsewhere.

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Notes and references

‡ All PND data collected at 298 K unless otherwise stated. Samples were loaded into V cans with In seals in a N_2-filled glovebox before data collection. Data were collected at 145, 90 and 35° detector banks. All compounds crystallise in hexagonal space group $R\bar{3}m$ with $Z = 3$, X occupying the 3a site, N the 3b site and Ca the 6c (0,0,*z*) site. Ca_2NCl, $M = 224.3$, $a = 3.6665(1)$, $c = 19.7187(2)$ Å, $V = 229.57(1)$ Å^3, z(Ca) = 0.2288(1), 12645 observations, 57 parameters, $R_{wp} = 2.93\%$, $R_p = 5.65\%$, $\chi^2 = 5.89$. $Ca_2N(Cl,Br)$, $M = 447.2$, $a = 3.6937(1)$, $c = 20.1780(2)$ Å, $V = 238.42(1)$ Å^3, z(Ca) = 0.2272(1), SOF(Cl) = 0.56(1), 12847 observations, 59 parameters, $R_{wp} = 2.26\%$, $R_p = 4.24\%$, $\chi^2 = 2.88$. Ca_2NBr, $M = 522.23$, $a = 3.7186(1)$, $c = 20.5668(1)$ Å, $V = 246.30(1)$ Å^3, z(Ca) = 0.2258(1), 12011 observations, 55 parameters, $R_{wp} = 2.31\%$, $R_p = 3.58\%$, $\chi^2 = 2.76$. $Ca_2N(Cl,Br)$ at 150 K, $a = 3.6871(1)$, $c = 20.1295(2)$ Å, $V = 236.99(1)$ Å^3, z(Ca) = 0.2273(1), 13090 observations, 54 parameters, $R_{wp} = 1.39\%$, $R_p = 2.31\%$, $\chi^2 = 3.32$. $Ca_2N(Cl,Br)$ at 75 K, $a = 3.6851(1)$, $c = 20.1130(1)$ Å, $V = 236.54(1)$ Å^3, z(Ca) = 0.2273(1), 12756 observations, 57 parameters, $R_{wp} = 1.43\%$, $R_p = 2.36\%$, $\chi^2 = 3.60$.

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