Preparation and Crystal Structures of the First Alkali-rich Sodium Aluminates $Na_7Al_3O_8$ and Na_5AlO_4

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Summary *X*-Ray crystal structure determinations of two sodium aluminates have shown Na_5AlO_4 (orthorhombic, space group *Pbca*) to contain discrete AlO_4 tetrahedra and $Na_7Al_3O_8$ (triclinic, $P\bar{1}$) to contain a novel ring structure made up of six AlO_4 tetrahedra which are linked by four oxygen bridges to form an infinite chain.

THE sodium oxide–aluminium(III) oxide system has been extensively studied, but no compounds have been reported for the sodium-rich end of the system. We have been interested in the reactions of Al_2O_3 with liquid sodium containing dissolved oxygen and as part of this study we undertook some solid state reactions of sodium oxide with Al_2O_3 The reaction of Na_2O with α-Al_2O_3 in the molar ratios of 7 : 3 and 5 : 1 at 700 °C for 18 h gave extremely hygroscopic white products. Microscopic examination of the products in an Ar-filled evacuable drybox revealed the presence of very small, irregularly shaped crystals in a powder matrix. In this paper we report two crystal structure determinations which show the reaction products to be the first sodium rich aluminates $Na_7Al_3O_8$ and Na_5AlO_4.

Crystal data: $Na_7Al_3O_8$, $M = 369{\cdot}9$; triclinic, space group $P\bar{1}$, $a = 7{\cdot}972$, $b = 5{\cdot}851$, $c = 11{\cdot}272$ Å, $\alpha = 89{\cdot}71$, $\beta = 110{\cdot}57$, $\gamma = 108{\cdot}99°$, $Z = 2$; $D_c = 2{\cdot}66$ g cm^{-3}; $F(000) = 360$; μ(Mo-$K_{\alpha(1)}$) = 7·91 cm^{-1}. The structure was refined to $R = 0{\cdot}0327$, $R_w = 0{\cdot}0361$ for 1569 independent reflections with intensities $I > 3\sigma(I)$ in the range $1 < \theta < 27°$. Na_5AlO_4, $M = 205{\cdot}9$; orthorhombic, space group *Pbca*, $a = 5{\cdot}894$, $b = 17{\cdot}870$, $c = 10{\cdot}095$ Å; $Z = 8$; $D_c = 2{\cdot}57$ g cm^{-3}; $F(000) = 800$; μ(Mo-$K_{\alpha(1)}$) = 7·38 cm^{-1}. The structure was refined to $R = 0{\cdot}034$, $R_w = 0{\cdot}037$ for 598 independent reflections with intensities $I > 3\sigma(I)$ in the range $1 < \theta < 25°$. Data were collected on a Hilger and Watts four circle diffractometer. For both compounds the initial atomic co-ordinates had to be found directly using the MULTAN 78 program.[1] This procedure correctly located the positions of 4Na, 2Al, and 5O atoms for $Na_7Al_3O_8$ and 4Na, and 3O atoms for Na_5AlO_4. Fourier syntheses phased on these atoms using the CRYSTALS program,[2] revealed the positions of all the remaining atoms in both compounds. After refinement, difference Fourier syntheses showed no significant peaks for $Na_7Al_3O_8$ or Na_5AlO_4.†

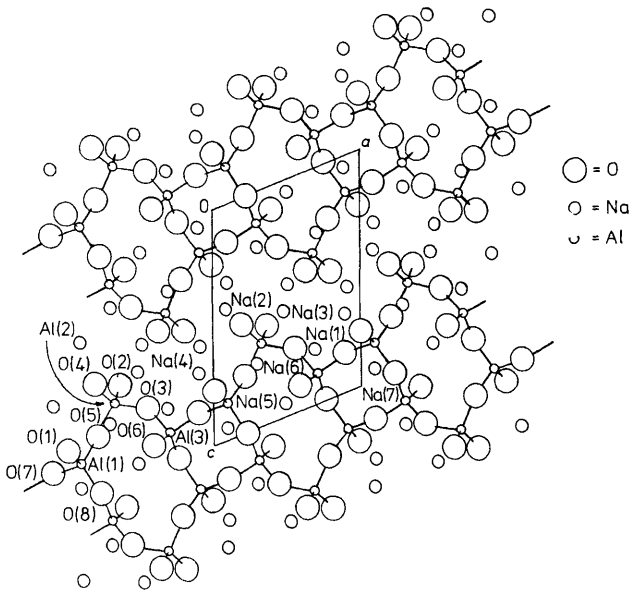

FIGURE 1. The crystal structure of $Na_7Al_3O_8$, viewed along the *b*-axis, showing the co-ordination of oxygen about aluminium. Bond lengths: O(7)–Al(1) = 1·769; O(1)–Al(1) = 1·734; O(5)–Al(2) = 1·79(8); O(8)–Al(1) = 1·77(6); O(5)–Al(2) = 1·7(8); O(4)–Al(2) = 1·74(0); O(3)–Al(2) = 1·79(8); O(2)–Al(2) = 1·74(7); O(3)–Al(3) = 1·75(6); O(6)–Al(3) = 1·73(0); O(7)–Al(3) = 1·76(1); O(8)–Al(3) = 1·77(9) Å. Selected angles are: O(8)–Al(1)–O(5) = 113·4(5); O(7)–Al(1)–O(5) = 103·4(5); O(8)–Al(1)–O(1) = 108·4(1); O(7)–Al(1)–O(1) = 110·9(6); O(5)–Al(1)–O(1) = 113·3(4); Al(1)–O(5)–Al(2) = 136·9(7); O(5)–Al(2)–O(3) = 108·4(0); O(5)–Al(2)–O(4) = 111·7(2); O(5)–Al(2)–O(2) = 109·4(4); O(4)–Al(2)–O(2) = 116·3(0); Al(2)–O(3)–Al(3) = 145·3(6); O(3)–Al(3)–O(6) = 114·5(5); O(6)–Al(3)–O(7) = 106·7(9); O(3)–Al(3)–O(8) = 107·2(3)°.

The compound $Na_7Al_3O_8$ has a basic framework built up of tetrahedral AlO_4 units sharing corners to form non-planar six-membered rings with Al–O bond lengths between 1·730 and 1·798 Å and bond angles between 103·4 and 145·4°. These rings are joined by two oxygen bridges to adjacent rings to form an infinite chain running parallel to the axis (Figure 1). This type of ring structure has not been previously observed in aluminates but has been proposed for the silicate $Na_2Ca_3[Si_6O_{16}]$.[3] The compound $Na_7Al_3O_8$ was found to be completely isostructural with the ternary oxide $Na_{14}[Fe_6O_{16}]$ which has recently been described.[4] Atomic positions are very similar for both compounds and both show an extremely complex co-ordination of the sodium atoms by oxygen, with Na–O distances between 2·27 and 2·65 Å.

The compound Na_5AlO_4 is composed of isolated AlO_4 tetrahedra with Al–O bond lengths between 1·761 and 1·789 Å and bond angles between 106·73 and 111·97°. The orientation of the tetrahedra is best considered with respect to the view shown in Figure 2.

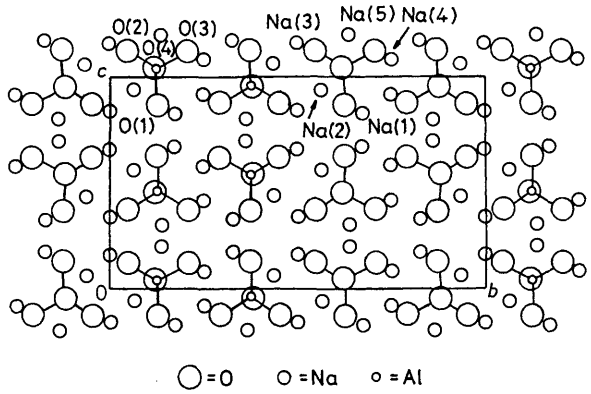

FIGURE 2. The crystal structure of Na_5AlO_4, viewed along the *a*-axis, showing the co-ordination of oxygen about aluminium. Bond lengths: O(1)–Al = 1·78(4); O(2)–Al = 1·76(8); O(3)–Al = 1·78(9); O(4)–Al = 1·76(1) Å. Bond angles: O(1)–Al–O(2) = 111·9(7); O(1)–Al–O(3) = 110·4(2); O(1)–Al–O(4) = 108·8(8); O(2)–Al–O(3) = 106·7(3); O(2)–Al–O(4) = 110·9(7); O(3)–Al–O(4) = 107·7(8)°.

Double rows with tetrahedra in the same vertical orientation run parallel to the *c*-axis. Within each row, adjacent tetrahedra are related by a reflection in the 001 plane, and adjacent tetrahedra in the *b*-axis direction are related by a 180 ° rotation about the *a*-axis, with or without a reflection

† The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, W. Germany. Any request should be accompanied by the full literature citation for this communication.

in the 100 plane. Each sodium atom has a four-fold co-ordination by oxygen with Na–O distances between 2·213 and 2·550 Å. The presence of isolated AlO_4 tetrahedra is not unique amongst aluminate structures having been observed in β-Li_5AlO_4;[5,6] Na_5AlO_4 is also isostructural with the corresponding ferrate Na_5FeO_4.[7]

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[1] MULTAN 78, A program for the automatic solution of crystal structures from X-ray diffraction data, P. Main, Dept. Physics, University of York, England.
[2] J. R. Carruthers, 'The Oxford Crystallographic Package—CRYSTALS.'
[3] I. Mayi, *Yogyo Kyokai Shi*, 1968, **76**, 203.
[4] G. Brachtel and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1978, **446**, 87.
[5] F. Stewner and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1971, **381**, 149.
[6] R. Hoppe and H. König, *Z. Anorg. Allg. Chem.*, 1977, **430**, 211.
[7] G. Brachtel and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1978, **446**, 77.