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# Structure of $Na_2Ba_3Cr_4F_{20}$

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**Abstract.** $M_r = 1045{\cdot}9$, monoclinic, $P2_1/n$, $a = 7{\cdot}262\ (4)$, $b = 20{\cdot}668\ (8)$, $c = 5{\cdot}431\ (2)$ Å, $\beta = 90{\cdot}76\ (1)°$, $V = 815{\cdot}1$ Å$^3$, $Z = 2$, $D_x = 4{\cdot}26$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 98{\cdot}9$ cm$^{-1}$, $F(000) = 931{\cdot}93$, room temperature, $R = 0{\cdot}027$, 1099 unique reflections. The structure is built from infinite *cis* $[MF_5^{2-}]$ chains of corner-sharing octahedra as in the $BaGaF_5$ structure. A valence-bond analysis shows that an $Na^+$ ion is mainly bonded to only one chain whereas the $Ba^{2+}$ ions ensure the connection between several chains.

**Introduction.** The only type of phase previously reported in the ternary systems Na–$BaF_2$–$MF_3$ is $NaBaM_2F_9$ ($M^{III}$ = Fe, Cr, Ga, Al) (de Kozak, Samouël, Leblanc & Ferey, 1982). It was recently found to crystallize (Ferey, Leblanc, de Kozak, Samouël & Pannetier, 1985) with the $Ba_2CoFeF_9$-type structure (de Kozak, Leblanc, Samouël, Ferey & De Pape, 1981).

This paper reports the single-crystal structure determination of a new phase of these ternary diagrams: $Na_2Ba_3Cr_4F_{20}$. Its one-dimensional structure is related to that of $BaCrF_5$ (Holler, Kurtz, Babel & Knop, 1982) and is compared with that of $NaBaM_2F_9$ in terms of a valence-bond analysis.

**Experimental.** Single crystal grown by heating the elementary fluorides at $T = 1173$ K in a platinum tube for 72 h. $D_m$ not determined. Green crystal $0{\cdot}210 \times 0{\cdot}045 \times 0{\cdot}045$ mm. Data collected on an automatic four-circle Philips PW 1100 diffractometer, $\theta$–$2\theta$ scan mode, sweep 1·40°, aperture 1·0°, scanning speed 0·03° s$^{-1}$. Cell parameters from 25 reflections. Absorption corrections by the Gauss method; $A_{max} = 0{\cdot}610$, $A_{min} = 0{\cdot}177$. Intensity measurement to $\theta_{max} = 25°$ within range $-9 \leq h \leq +9$, $0 \leq k \leq 25$, $-6 \leq l \leq +6$; standard reflections $\bar{1}41$, $1\bar{4}1$, $\bar{2}1\bar{1}$, intensity variation 2·5%; 2310 reflections measured, 579 rejected $[\sigma(I)/I > 0{\cdot}5]$, 1099 unique $[|F|/\sigma(|F|) > 6{\cdot}0]$, $R_{int} = 0{\cdot}034$. Structure solved from tangent method. $F$ magnitudes used in least-squares refinements; unit weights; 134 parameters refined; mean $\Delta/\sigma = 0{\cdot}013$, max. = 0·080; secondary-extinction factor $g = 2{\cdot}60\ (9) \times 10^{-7}$. Atomic scattering factors for $Na^+$, $Ba^{2+}$, $Cr^{3+}$, $F^-$ and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); calculations with *SHELX*76 program (Sheldrick, 1976); max. and min. heights in final $\Delta F$ map: 1·1 and −0·9 e Å$^{-3}$.

**Discussion.** The final atomic coordinates and the equivalent isotropic temperature factors are listed in Table 1.† Projections of the structure along [001] and [010] appear in Figs. 1 and 2, respectively.

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† Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42409 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The structure of $Na_2Ba_3Cr_4F_{20}$ is built from infinite *cis* $[CrF_5^{2-}]$ chains of corner-sharing octahedra between which $Na^+$ and $Ba^{2+}$ ions are inserted. The mean Cr—F distances (Table 2) are very close to the sum of the $Cr^{3+}$ and $F^-$ ionic radii (1·90 Å) (Shannon, 1976). However, the $CrF_6$ octahedra are somewhat distorted with two long Cr—F(4) and Cr—F(8) bond lengths. These bridging F(4) and F(8) ions connect the adjacent metallic octahedra within the chains; the other $F^-$ ions of the octahedra are terminal. The mean Na—F and Ba—F distances do not depart from the sum of the ionic radii, 2·61 and 2·87 Å respectively (Shannon, 1976). The $Na^+$ and $Ba^{2+}$ cations are respectively 9 and 12 coordinated to $F^-$ ions (Table 2). However, $Na^+$ and $Ba^{2+}$ ions do not participate equally in the connection of the $[CrF_4F_{2/2}]_n^{2n-}$ chains. A bond-valence analysis (Table 3) shows that an $Na^+$ ion is firmly tied to only one chain of octahedra: 63% of the $Na^+$ valence is shared with F(1), F(2), F(4), F(8), F(9) located in the same chain (Fig. 1). In contrast, the Ba(1) and Ba(2) valences are shared almost equally with $F^-$ ions of three or four chains respectively. A similar peculiarity is found in the structure of $NaBaM_2F_9$ ($M$ = Fe, Cr), recently described (Ferey *et al.*, 1985): an $Na^+$ ion is inserted in only one double *trans* chain of octahedra, whereas the $Ba^{2+}$ ions link these double chains together, constituting the structure. The isolated *cis* $[MF_5^{2-}]$ chains of octahedra found in the structure of $Na_2Ba_3Cr_4F_{20}$ were previously reported only for $BaGaF_5$ (Domesle & Hoppe, 1978), $BaCrF_5$ (Holler *et al.*, 1982) and $Rb_2CrF_5$ (Jacoboni, De Pape, Poulain, Le Marouille & Grandjean, 1974).

Table 1. *Fractional coordinates and equivalent isotropic temperature factors* (Å$^2$) *in* $Na_2Ba_3Cr_4F_{20}$, *with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}\sum_i\sum_j B_{ij}(\mathbf{a}_i.\mathbf{a}_j)$ (Hamilton, 1959). Equivalent positions: $x, y, z; -x, -y, -z; \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Na(1) | 0·7736 (5) | 0·4094 (2) | −0·0139 (6) | 1·86 (15) |
| Ba(1) | 0 | 0 | 0 | 1·12 (3) |
| Ba(2) | 0·4947 (1) | 0·2769 (1) | −0·4763 (1) | 0·90 (2) |
| Cr(1) | 0·4675 (2) | 0·1386 (1) | −0·0270 (2) | 0·67 (5) |
| Cr(2) | 0·2879 (2) | 0·3965 (1) | −0·0192 (2) | 0·65 (5) |
| F(1) | 0·2957 (6) | 0·1791 (2) | −0·2407 (8) | 1·21 (20) |
| F(2) | 0·3072 (6) | 0·0677 (2) | 0·0009 (9) | 1·64 (18) |
| F(3) | 0·2730 (6) | 0·3065 (2) | −0·0498 (9) | 1·53 (20) |
| F(4) | 0·1447 (6) | 0·4066 (2) | −0·3199 (8) | 1·51 (20) |
| F(5) | 0·3116 (6) | 0·4870 (2) | −0·0014 (9) | 1·57 (21) |
| F(6) | 0·4998 (6) | 0·3929 (2) | −0·2168 (8) | 1·11 (18) |
| F(7) | 0·6260 (6) | 0·2103 (2) | −0·0621 (9) | 1·40 (20) |
| F(8) | 0·5674 (6) | 0·0991 (2) | −0·3246 (8) | 1·20 (19) |
| F(9) | 0·8566 (6) | 0·3220 (2) | −0·2550 (8) | 1·27 (20) |
| F(10) | 0·9351 (6) | 0·1112 (2) | −0·2352 (8) | 1·31 (20) |

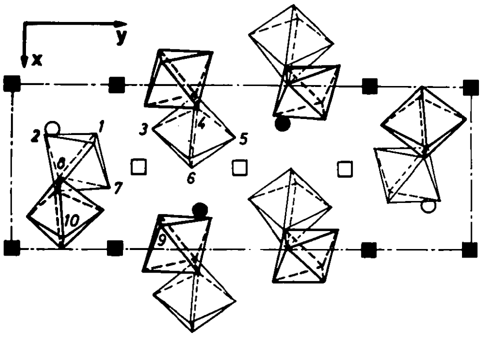

Fig. 1. [001] projection of the structure of $Na_2Ba_3Cr_4F_{20}$. Full and open symbols refer to $z \approx 0$ and $z \approx \frac{1}{2}$, respectively. Na is represented by circles and Ba by squares; F are numbered as in Table 1.

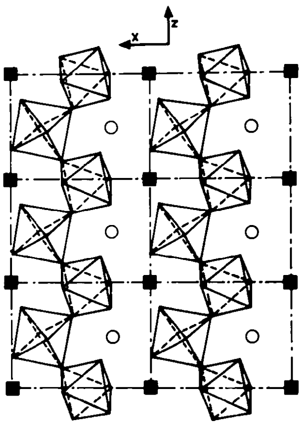

Fig. 2. [010] projection of the structure of $Na_2Ba_3Cr_4F_{20}$.

The authors are very indebted to Dr J. Pannetier for the valence-bond calculations.

Table 2. *Selected bond lengths* (Å) *and angles* (°) *in* $Na_2Ba_3Cr_4F_{20}$

E.s.d.'s for distances and angles are 0·006 Å and 0·1°, respectively.

| | | | |
|---|---|---|---|
| Cr(1)—F(1) | 1·889 | Cr(2)—F(3) | 1·871 |
| Cr(1)—F(2) | 1·879 | Cr(2)—F(4) | 1·936 |
| Cr(1)—F(4) | 1·938 | Cr(2)—F(5) | 1·881 |
| Cr(1)—F(7) | 1·887 | Cr(2)—F(6) | 1·889 |
| Cr(1)—F(8) | 1·959 | Cr(2)—F(8) | 1·933 |
| Cr(1)—F(9) | 1·878 | Cr(2)—F(10) | 1·872 |
| ⟨Cr(1)—F⟩ = 1·905 | | ⟨Cr(2)—F⟩ = 1·897 | |
| 2Ba(1)—F(2) | 2·633 | Ba(2)—F(1) | 2·803 |
| 2Ba(1)—F(4) | 3·377 | Ba(2)—F(1′) | 2·784 |
| 2Ba(1)—F(5) | 3·043 | Ba(2)—F(3) | 2·903 |
| 2Ba(1)—F(5′) | 3·062 | Ba(2)—F(3′) | 2·690 |
| 2Ba(1)—F(6) | 2·695 | Ba(2)—F(3″) | 3·540 |
| 2Ba(1)—F(10) | 2·668 | Ba(2)—F(6) | 2·782 |
| | | Ba(2)—F(7) | 2·794 |
| ⟨Ba(1)—F⟩ = 2·913 | | Ba(2)—F(7′) | 2·794 |
| | | Ba(2)—F(7″) | 3·606 |
| | | Ba(2)—F(9) | 3·023 |
| | | Ba(2)—F(9′) | 2·727 |
| Na(1)—F(1) | 2·360 | Ba(2)—F(10) | 2·739 |
| Na(1)—F(2) | 2·692 | | |
| Na(1)—F(2′) | 2·843 | ⟨Ba(2)—F⟩ = 2·932 | |
| Na(1)—F(4) | 3·186 | | |
| Na(1)—F(5) | 2·230 | | |
| Na(1)—F(6) | 2·286 | Cr(1)—F(4)—Cr(2) | 137·7 |
| Na(1)—F(8) | 2·362 | Cr(1)—F(8)—Cr(2) | 133·3 |
| Na(1)—F(9) | 2·316 | | |
| Na(1)—F(10) | 2·934 | | |
| ⟨Na(1)—F⟩ = 2·579 | | | |

Table 3. *Valence-bond analysis of* $Na_2Ba_3Cr_4F_{20}$; *s values from Zachariasen's* (1978) *equation; valence-bond parameters from Ferey et al.* (1985)

| | Na | Ba(1) | Ba(2) | Cr(1) | Cr(2) | $\sum s$ |
|---|---|---|---|---|---|---|
| F(1) | 0·149 (1) | | 0·193 (2)<br>0·209 (3) | 0·503 (7) | | 1·054 (13) |
| F(2) | 0·081 (1)<br>0·058 (1) | 2 × 0·286 (1) | | 0·541 (8) | | 0·966 (12) |
| F(3) | | | 0·026 (1)<br>0·156 (2)<br>0·250 (3) | | 0·551 (8) | 0·983 (13) |
| F(4) | 0·034 (1) | 2 × 0·045 (1) | | 0·445 (6) | 0·432 (6) | 0·956 (14) |
| F(5) | 0·188 (2) | 2 × 0·093 (1)<br>2 × 0·104 (1) | | | 0·541 (7) | 0·926 (11) |
| F(6) | 0·165 (1) | 2 × 0·245 (3) | 0·194 (2) | | 0·561 (8) | 1·165 (14) |
| F(7) | | | 0·026 (1)<br>0·177 (2)<br>0·218 (2) | 0·539 (7) | | 0·960 (12) |
| F(8) | 0·140 (1) | | | 0·451 (6) | 0·500 (7) | 1·091 (14) |
| F(9) | 0·167 (1) | | 0·098 (1)<br>0·214 (3) | 0·575 (8) | | 1·054 (13) |
| F(10) | 0·053 (1) | 2 × 0·257 (3) | 0·213 (3) | | 0·519 (7) | 1·042 (14) |
| $\sum s$ | 1·03 (1) | 2·06 (4) | 1·97 (3) | 3·05 (4) | 3·10 (4) | |
| $\sum s$ (expected) | 1 | 2 | 2 | 3 | 3 | |

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# Structure of an Aluminosilicophosphate

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**Abstract.** $H_3O^+.Al_4SiP_3O_{16}^-.nH_2O$, $M_r = 503·9 + (n \times 18)$, trigonal, $R3$, $a = 13·781$ (1), $c = 14·846$ (2) Å, $V = 2441·7$ (5) Å$^3$, $Z = 4·5$, $D_m = 1·92$ (2), $D_x = 1·54$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·7107 Å, $\mu$(Mo $K\alpha$) = 0·584 mm$^{-1}$, $F(000) = 1125$, $T = 298$ (2) K, final $R = 0·067$ for 1011 unique observed reflections. The structure is related to that of chabazite, and is formed by joining together four-, six- and eight-membered rings of $AlO_4$ and $(P,Si)O_4$ tetrahedra. There are large ellipsoidal cavities linked by 2 six-membered-, 6 eight-membered- and 12 four-membered-ring apertures.

**Introduction.** Several aluminosilicophosphate molecular sieves have been synthesized recently (Lok, Messina, Patton, Gajek, Cannan, & Flanigen, 1984); these possess important and unique properties suitable for adsorptive, catalytic and ion-exchange applications. However, there has been no report on the crystal structure of this new family of aluminosilicophosphate molecular sieves. In this paper, the crystal structure of $H_3O^+.Al_4SiP_3O_{16}^-.nH_2O$ (ZYT-6) is reported.

**Experimental.** The crystals were prepared hydrothermally from the gel composed of $P_2O_5/Al_2O_3$/morpholine/$SiO_2$ with molar ratio 1:1:2:1. The calculated density of the crystal is small in comparison with the measured density (flotation in aqueous $ZnI_2$); the discrepancy results from the presence of a large amount of zeolitic water in the cavities. Colorless prismatic crystals were obtained and used for the X-ray work. Atomic-absorption and ICP (inductively coupled plasma) spectrometry showed that the crystals contained P 15·1, Al 18, Si 4·12, Na 0·07 wt%, indicating that the composition of the crystal is $Al_{4.0}P_{2.92}Si_{0.88}O_{15.6}.nH_2O$. Small fragments from the chemical analysis are not reliable, and the composition was assumed to be $H_3O^+.Al_4SiP_3O_{16}^-.nH_2O$. Approximate dimensions of the crystal specimen 0·20 × 0·15 × 0·15 mm. Rigaku

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