Synthesis and Structure of a New Germanate Fluoride: NaCa$_2$GeO$_4$F[1]

L. F. Schneemeyer,[2] Lila Guterman, T. Siegrist, and G. R. Kowach

Bell Laboratories, Lucent Technologies, 600 Mountain Avenue Murray Hill, New Jersey 07974

We report the synthesis and structural characterization of a new oxoanion halide, NaCa$_2$GeO$_4$F. Crystal data: FW = 235.74, *Pnma* (No. 62), orthorhombic, $a = 5.362(2)$, $b = 7.328(3)$, $c = 12.681(4)$ Å, $V = 498.3(3)$ Å^3, $Z = 4$, $R(F) = 0.044$, $R_w(F) = 0.046$ for 404 averaged reflections. Compositionally, this material can be viewed as the end-member of the hypothetical solid solution Ca$_2$GeO$_4$ · (CaO)$_{1-x}$ · (NaF)$_x$. However, in this unusual oxyfluoride, the fluoride ion orders and fully occupies one anion site. The structure consists of complicated condensed chains of six-coordinated cations centered by fluoride ions and linked by chains of isolated germanium oxide tetrahedra. The structure is best described in terms of the anion packing rather than the packing of cation-centered coordination polyhedra.
© 2001 Academic Press

INTRODUCTION

While the solid state chemistry of both oxides and fluorides is extensive, mixed oxoanion fluorides have received much less attention. Typically, oxyfluorides have had the same structures as most of the simple oxides or fluorides; common structures include rutile and fluorite, or structures typical of complex oxides or fluorides such as pyrochlore or garnet. In most oxyfluorides, there is a random arrangement of O and F in the anion positions; ordered arrangements in oxyfluorides including superstructures are more rare (1). Recent examples of new crystalline mixed oxoanion fluorides include a potential new phosphor host, Sr$_2$LiSiO$_4$F (2), new ferroelectrics and ferroelectric relaxors such as Ba(Ti$_{1-x}$Li$_x$)O$_{3-3x}$F$_{3x}$ (3), new mixed anion bronzes such as K$_{0.23}$V$_2$O$_{4.77}$F$_{0.23}$ (4), and cuprate superconductors like that with $T_c = 85$ K, Sr$_2$LaCu$_2$O$_5$F (5). Not surprisingly, interesting anion arrangements such as those found in a mixed oxoanion fluoride can affect the optical or electronic properties of the resulting material.

Mixed anion phases may play a role in dissolution, which is important for molten salt flux systems. The nature of dissolved species in molten salt fluxes has long been a subject of both investigation and speculation. Greater insights into the types of cluster units that form in high-temperature molten salts might allow more rational choices of suitable flux systems for the growth of desired crystalline materials. Generally, it has been assumed that the soluble species are fragments of the parent compound, which exist as ions or cluster units. Alternatively, though, the soluble species might involve intermediates formed by the reaction of the solute material with the solvent flux. Alkali halides, particularly alkali fluorides, have been widely employed for the flux growth of a large number of oxides (6). Materials as diverse as CoO, FeF$_2$, and Bi$_2$Sr$_2$CaCu$_2$O$_8$ have been grown from alkali halide fluxes. In this paper, we describe the growth and X-ray characterization of single crystals of a new oxo-anion halide, NaCa$_2$GeO$_4$F. This material, whose composition may also be written NaF · Ca$_2$GeO$_4$, has an ordered anion arrangement and may represent an example of a solution species present in a molten fluoride flux.

EXPERIMENTAL

Sample Preparation

Clear, colorless, euhedral crystals of typical size 0.5 mm were grown from a peritectic decomposition of a prereacted stoichiometric ceramic preparation. The material was ground together thoroughly using an agate mortar and pestle, placed in a platinum crucible and subsequently heated to 950°C then cooled at 15°C/h to 890°C in a flowing nitrogen atmosphere. The resulting sample appeared melted with chunky crystals coating the surface. Single crystals were selected from the product using a microscope. A homogeneous powder of the NaCa$_2$GeO$_4$F compound was prepared by grinding together a stoichiometric mixture in an agate mortar and pestle, then firing at 850°C for 12 h in a flowing nitrogen atmosphere. The resulting powder was reground, pressed into a pellet, and heated again to 850°C for 12 h. Powder X-ray diffraction confirmed a nearly single phase product.

[2] To whom correspondence should be addressed.

TABLE 1
Crystal Data and Intensity Collection for NaCaGeO$_4$F

Formula	NaCaGeO$_4$F
Formula weight	235.74
Space group	*Pnma*
Crystal size	$0.11 \times 0.01 \times 0.12$ mm^3
a	5.362(2) Å
b	7.328(3)
c	12.681(4) Å
V (Å^3)	498.3(3)
Z	4
D_c (g/cm^3)	3.143
μ (MoKα) (cm^{-1})	262.3
Diffractometer	Nonius CAD4
Radiation	(MoKα)($\lambda = 0.71069$ Å) graphite-monochromated
Temperature	23°C
$2\theta_{MAX}$	120°
Data collected	1682
Scan type	$\theta/2\theta$
Independent reflections	404
Reflections measured $(I > 2.5\sigma(I))$	376
R	0.044
R_w ($w = 1/\sigma^2(F_o)$)	0.045
Extinction length (μm)	0.373(32)

Structure Determination

A cuboctahral-shaped crystal was measured at 23°C on an Enraf–Nonius CAD-4 diffractometer using graphite monochromatized MoKα radiation and the NRCCAD program package (7). All calculations were carried out on a Sun workstation using the NRCVAX structure package (8). Although fluorine and oxygen differ by only a single electron, atom positions were distinguished based on crystal chemical considerations and isomorphism. Lattice parameters were determined from the absolute 2θ values of reflections at high angle, 25 reflections with $60° < 2\theta < 65°$. An absorption correction was applied to all measured intensities using a Gaussian integration absorption correction. Anisotropic temperature factors for all atoms were included in the final refinements. Crystallographic data are listed in Table 1, atomic coordinates and isotropic thermal parameters in Table 2, and selected bond lengths in Table 3.

The phase, NaCa$_2$GeO$_4$F, crystallizes in an orthorhombic space group, *Pnma*, with $a = 5.362(2)$, $b = 7.328(3)$, and $c = 12.681(4)$ Å. This corresponds well to the powder X-ray diffraction pattern for stoichiometric ceramic material as shown in Table 4. Lattice constants ($a = 5.358(2)$, $b = 7.324(2)$, $c = 12.685(4)$ Å) obtained from powder X-ray diffraction data of indexed reflections up to 60° in 2θ agree with the lattice constants measured for the single crystal.

DESCRIPTION OF THE STRUCTURE

The NaCa$_2$GeO$_4$F structure contains chains of edge-sharing MO_6 octahedra (where M is the shared Ca and Na site) running along the a direction, which are linked by GeO$_4$ tetrahedra as shown in Figs. 1 and 2a and 2b. Although the M sites are crystallographically inequivalent, the coordination geometry is strikingly similar (Fig. 3). The distorted octahedral coordination displays the cation off-center with slightly longer cation–fluorine bond lengths as

TABLE 2
Atomic Parameters x, y, z and Biso for NaCa$_2$GeO$_4$F

	x	y	z	B_{iso}	occ
Ge	0.8028(3)	$\frac{3}{4}$	0.08338(10)	1.12(7)	
O1	0.1299(17)	$\frac{3}{4}$	0.0814(7)	1.8(4)	
O2	0.7051(13)	0.5545 (9)	0.1486(5)	2.3(3)	
O3	0.3013(20)	$\frac{1}{4}$	0.0484(6)	2.1(4)	
F	0.0008(14)	$\frac{1}{4}$	0.2405(6)	1.8(3)	
Ca1*	0.2636(4)	0.4900(3)	0.17030(15)	1.62(9)	0.70(2)
Ca2*	0.7338(6)	$\frac{1}{4}$	0.09083(22)	1.48(13)	0.73(2)

	$u11(U)$	$u22$	$u33$	$u12$	$u13$	$u23$
Ge	2.48(10)	1.19(8)	0.60(8)	0.0	0.01(6)	0.0
O1	2.7(5)	2.7(5)	1.7(4)	0.0	0.3(4)	0.0
O2	5.6(4)	1.8(3)	1.5(3)-	0.9(3)	− 0.5 (3)	0.6(3)
O3	5.1(6)	2.6(5)	0.1(4)	0.0	− 0.1(4)	0.0
F	2.7(4)	2.3(4)	2.0(4)	0.0	0.3(4)	0.0
Ca1	3.49(13)	1.75(11)	0.90(10)	0.00(10)	0.10(9)	− 0.07(8)
Ca2	3.36(19)	1.49(15)	0.78(14)	0.0	− 0.07(14)	0.0

Note. B_{iso} is the mean of the principal axes of the thermal ellipsoid. E.S.Ds. refer to the last digit printed. Anisotropic temperature factors are of the form Temp $= -2\pi^2(h*h*u11*a^2 + \cdots + 2*h*k*u12*a**b* + \cdots)$.

TABLE 3
Selected Bond Distances for NaCa₂GeO₄F

Bond		Distance (Å)
Ca_1	O_1	2.32688
	O_2	2.42978
	O_2	2.36521
	O_3	2.35044
	F	2.42323
	F	2.44732
Ca_2	O_1	2.30332
	O_2	2.35391
	O_2	2.35391
	O_3	2.38096
	F	2.37741
	F	2.47699
Ge	O_1	1.75414
	O_2	1.73514
	O_2	1.73514
	O_3	1.76141
O_1	Ca_1	2.32688
	Ca_1	2.32688
	Ca_2	2.30332
	Ge	1.75414
O_2	Ca_1	2.42978
	Ca_1	2.36521
	Ca_2	2.35391
	Ge	1.73514
O_3	Ca_1	2.35044
	Ca_1	2.35044
	Ca_2	2.38096
	Ge	1.76141
F	Ca_1	2.42323
	Ca_1	2.44732
	Ca_1	2.42323
	Ca_1	2.44732
	Ca_2	2.37741
	Ca_2	2.47699

compared to the cation–oxygen bond lengths. The average M–F bond distance (2.432 Å) is slightly longer than the average M–O bond distance (2.354 Å). Comparison of Shannon's ionic radii (9) would suggest that the opposite trend should be observed (M–O, 2.39 Å; M–F, 2.34 Å). Even though the M site is simultaneously occupied by Na^+ and Ca^{2+}, bond distance comparisons can be made due to the fact that the ionic radii are quite similar (1.00 for Na^+ and 1.02 for Ca^{2+} in octahedral coordination). We note that the oxygen ion occupies the tetrahedral site, bonding to three M cations and one germanium ion. The germanium–oxygen bond distance is short as expected at 1.746 Å on average.

Considering the anion coordination geometry is revealing. The fluorine is located in octahedral coordination (FM_6, m site symmetry). These fluorine-centered octahedra condense via face sharing to form chains along the a direction, as shown in Fig. 4. The faces of these octahedra are capped by face-shared oxygen-centered tetrahedra.

Isolated GeO_4 tetrahedra lying in m symmetry sites link the structure by vertex-shared oxygens. The GeO_4 tetrahedra are symmetry related by an inversion center, thus rendering the structure centrosymmetric. The range of bond lengths is 1.741 to 1.784 Å in $CaMgGeO_4$. These bond lengths are similar in $NaCa_2GeO_4F$, which has bond lengths in the range 1.735 to 1.761 Å.

The $NaCa_2GeO_4F$ structure can be formally related to a hexagonal perovskite structure (ABX_3) such as $BaNiO_3$ (10), where F sits in the octahedrally coordinated B site, the GeO_4 tetrahedron sits in the 12-coordinate (dodecahedral) A site, and the cations (NaCa2) take the place of the oxygens. Indeed, the fluorine is coordinated by six (Ca, Na), which share faces to form columns. While the center of gravity of the GeO_4 tetrahedra are located in the corresponding Ba locations, the orientation of the tetrahedra reduces the overall symmetry from hexagonal for $BaNiO_3$ to orthorhombic for $NaCa_2GeO_4F$. Still, the hexagonal symmetry is very pronounced in the structure, and orientational disorder of the GeO_4 tetrahedra could in principle lead to an overall hexagonal structure.

Unlike most alkaline earth germanium germinates and silicates (e.g., Ca_3GeO_5, Ca_3SiO_5, and $Ca_{3-x}GeO_4$ $(O_{1-2x}F_{2x})$), the $NaCa_2GeO_4F$ phase forms an ordered anion network. This ordering is also seen in the isomorphous phase, $NaCa_2SiO_4F$ (11), which is a component of concrete. The anion ordering is important in the solid state

TABLE 4
Powder Diffraction Data for NaCa₂GeO₄F

| Reflection (hkl)	d_{obs} (Å)	$2\theta_{obs}$ (°)	I/I_0 (%)
101	4.880	18.164	3
102, 111	4.089	21.718	28
013, 020	3.659	24.307	30
112	3.569	24.927	10
004, 022	3.171	28.121	66
121	2.941	30.369	6
104, 122	2.729	32.790	100
200	2.679	33.415	46
114	2.557	35.064	11
211, 202	2.468	36.379	7
131, 124, 115	2.188	41.221	2
033, 006	2.113	42.753	6
132	2.097	43.103	5
222, 204	2.047	44.204	59
133, 106	1.966	46.126	11
223	1.927	47.115	5
040, 026	1.831	49.763	88
230	1.805	50.516	2
231, 224, 215	1.787	51.079	3
141, 107	1.717	53.306	4
312	1.673	54.830	11
216	1.619	56.808	4
008, 044	1.586	58.120	8
322, 304	1.556	59.332	21
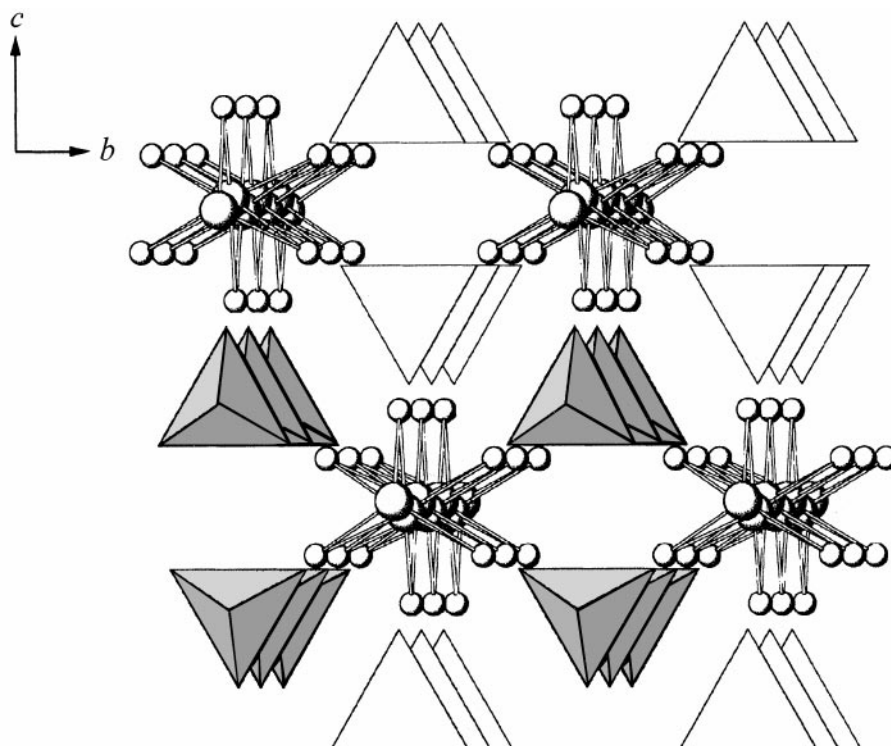
FIG. 1. View of the $NaCa_2GeO_4F$ structure down the a axis showing the chains of isolated GeO_4 tetrahedra. The other notable structural feature is the bonding within chains of face-shared fluorine-centered octahedra. The other notable structural feature is the bonding within chains of face-shared fluorine-centered octahedra formed by the calcium/sodium ions. Large spheres represent fluorine atoms, small spheres represent the mixed metal cation site, and germanium resides at the center of the tetrahedra with oxygen atoms at the vertices.
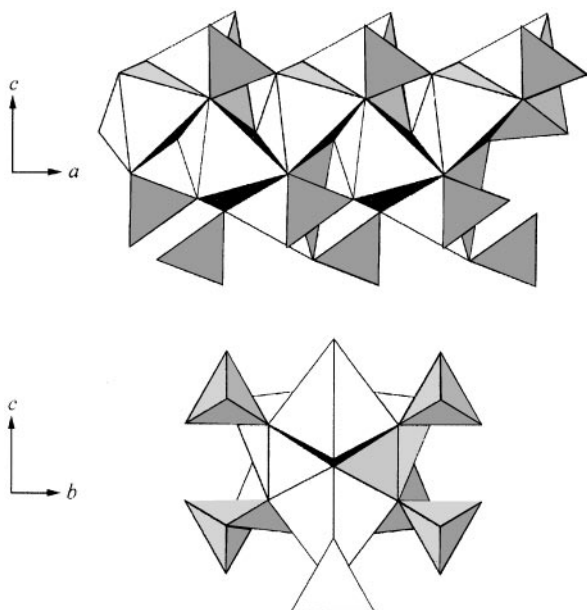

FIG. 2. Polyhedral representation of the $NaCa_2GeO_4F$ structure showing Ge in tetrahedral coordination and the mixed cation (Na and Ca) in octahedral coordination. View (a) is a projection in the a–c plane. Zig–zag chains of edge-shared octahedra lie along the a direction and are bridged by GeO_4 tetrahdra. View (b) is the projection down the a axis and shows the relative pseudo-hexagonal arrangement of the GeO_4 tetrahedra.

chemistry of this material which can formally be viewed as the end member of the solid solution, $Ca_2GeO_4 \cdot (CaO)_{1-x}(NaF)_x$. No intermediate compositions in this hypothetical solid solution can be formed, possibly because the drive to F ordering impedes their formation.

DISCUSSION

Crystal structures are usually discussed in terms of the cation coordination polyhedra, their packing, and the linkages between them. The tetrahedron and octahedron have important roles in many structural descriptions because they are the stable arrangements of four or six ions, respectively, around one of opposite charge. For example, a description of the perovskite structure often discusses MO_6 octahedra, where M is a small cation and O is oxygen, which link by corner sharing to form a cubic network.

One ubiquitous structure not commonly considered in terms of cation polyhedral packing is the spinel structure. Instead, most discussions of the structural arrangement in spinel begin with the anion arrangement; this spinel example contains a hexagonally packed anion net. The discussion of the spinel structure then goes on to describe the holes in the anion net that are occupied by cations to
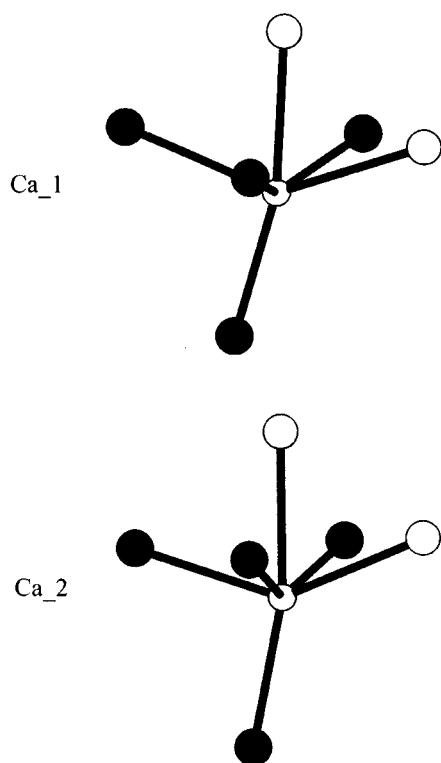
FIG. 3. Coordination environments for the cation sites, those occupied by disordered Na and Ca. In simplest concept, the cations occupy 6-coordinate, highly distorted octahedral sites. Filled circles represent oxygen atoms and open circles represent fluorine atoms.

FIG. 4. A view of the anion packing environment showing a polyhedral representation of the face-shared fluorine-centered octahedra in the a–c plane.

produce a material of interest. In the spinel structure, the cation polyhedra clearly show magnesium and aluminum in tetrahedral and octahedral coordination with oxygen, respectively. These tetrahedra are isolated within the structure while the octahedra are edge sharing. Considering instead the anion polyhedral packing illustrates all oxygen coordination as highly distorted tetrahedra. Pairs of edge-sharing tetrahedra link three-dimensionally via vertex sharing. In general, complex structures can easily be understood by considering both the packing of the cation and anion polyhedra.

The success of some molten salt solvent systems has been related to their tendency toward complex formation. Other factors such as melting temperature, volatility and viscosity are certainly important as well. Spectroscopic evidence for groups having well-defined symmetry in molten salt fluxes has been reported, particularly for transition metal ions (12). Structural evidence for such species was reported recently by Hedden *et al.* (13), who showed that the flux serves as an important reactant in the synthesis reaction of M'-RTaO$_4$ (R = Gd, Y, Lu) X-ray phosphors. In their study, powder X-ray diffraction clearly showed the formation of a rare-earth oxy-sulfate as a reaction intermediate.
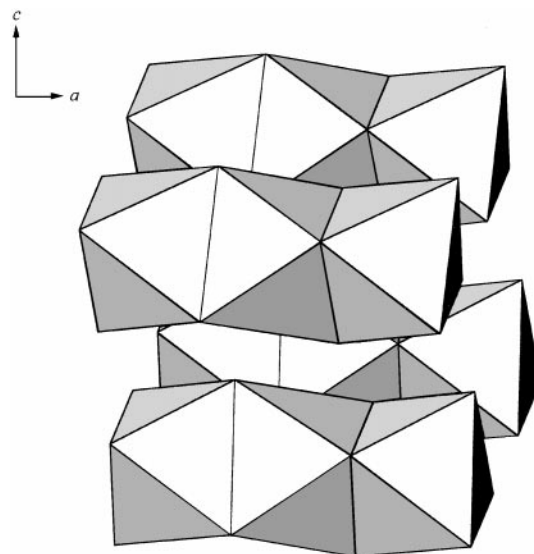
SUMMARY

A new oxo-anion halide, NaCa$_2$GeO$_4$F, has been grown and characterized using X-ray diffraction. This material can be viewed as the end-member of the hypothetical solid solution Ca$_2$GeO$_4 \cdot$(CaO)$_{1-x} \cdot$(NaF)$_x$. However, in this unusual oxyfluoride, the fluoride ion orders and fully occupies one anion site. Structural features include complicated condensed chains of six-coordinated cations centered by fluoride ions which are linked by chains of isolated germanium oxide tetrahedra. The structure is best described in terms of the anion packing rather than the packing of cation-centered coordination polyhedra. This phase may provide new insights into types of chemical species that are present in fluxes during crystal growth from molten salts.

ACKNOWLEDGMENT

REFERENCES

1. A. F. Wells, "Structural Inorganic Chemistry," Fourth ed., p. 500. Clarendon Press, Oxford, 1975.
2. A. Akella and D. A. Keszler, *Chem. Mater.* **7,** 1299 (1995).
3. J. Ravez and A. Simon, *Phys. Status Solidi A* **159,** 517 (1997)
4. Z. Ladjeroud, L. Benziada, and J. Ravez, *J. Fluorine Chem.* **70,** 163 (1995).
5. M. Isobe, J. Q. Li, Y. Matsui, and F. Izumi, *Physica C* **269,** 5 (1996).

6. D. Elwell and H. J. Scheel, "Crystal Growth from High Temperature Solutions." Academic Press, New York, 1975.

7. Y. LePage, P. S. White, and E. J. Gabe, *in* "Proc. Am. Crystallogr. Assoc. Annual Meeting," 1986 Hamilton, Canada, AIP, New York, 1986, Poster PA23.

8. E. J. Gabe, Y. Le Page, J.-P. Charland, F. L. Lee, and P. S. White, *J. Appl. Crystaalogr.* **22,** 384 (1989).

9. R. D. Shannon, *Acta Crystallogr. Sect. A*: *Found. Crystallogr.* **32,** 751 (1976).

10. J. J. Lander, *Acta Crystallogr.* **4,** 148 (1951).

11. Ö. Andac, F. P. Glasser, and R. A. Howe, *Acta Crystallogr. Sect. C*: *Cryst. Struct. Commun.* **53,** 831 (1997).

12. H. Bloom and W. Hastie, *in* "Non-aqueous Solvent Systems," (T. C. Waddington, Ed.). Academic Press, New York, 1965.

13. D. B. Hedden, C. C. Torardi, and W. Zegarski, *J. Solid State Chem.* **118,** 419 (1995).