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ORIGINAL PAPER

Hydrothermal Synthesis and Crystal Structure of Hexafluorogallate, Na_3GaF_6

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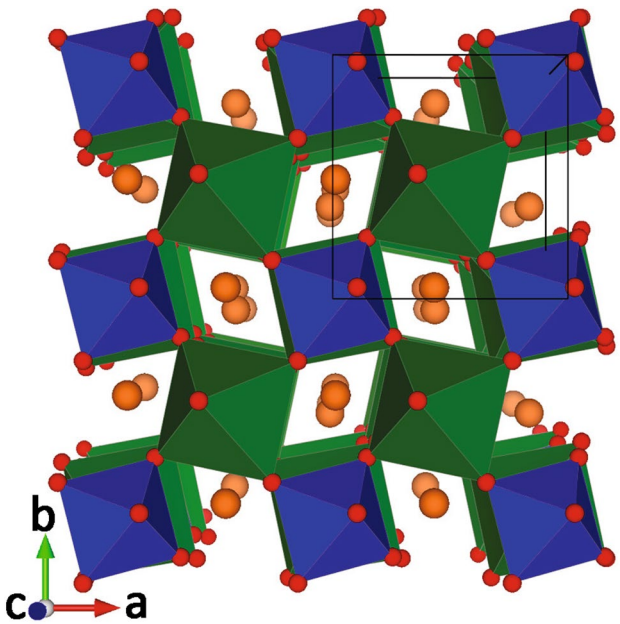
Abstract Single crystals of Na_3GaF_6 were prepared via a mild hydrothermal method and the crystal structure was characterized by single crystal X-ray diffraction. Na_3GaF_6 crystallizes in the monoclinic space group $P2_1/n$ with $a = 5.4724(3)$ Å, $b = 5.6742(3)$ Å, $c = 7.8866(4)$ Å, $\gamma = 90.361(1)^\circ$, $V = 244.89(2)$ Å^3, and $Z = 2$. The compound exhibits a cryolite-type crystal structure consisting of corner-shared GaF_6 and $Na(1)O_6$ polyhedra. The Ga and Na(1) atoms are found in almost regular octahedra, whereas the Na(2) atom is observed in a highly distorted square antiprismatic coordination environment.

Graphical Abstract The synthesis and crystal structure of the hexafluorogallate, Na_3GaF_6 is reported.



Keywords Crystal growth · Crystal structure · Hydrothermal synthesis · Na_3GaF_6

Introduction

Materials belonging to a cryolite-type structure, A_3BF_6 (A = monovalent and B = trivalent cations), have been continuously investigated due to not only their important function as host materials for luminescence ions, but also interesting structural phase transitions [1–3]. While many

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Table 1 Crystal data and structure refinement for Na_3GaF_6

Empirical formula	Na_3GaF_6
Color/shape	Colorless/polyhedral
Crystal size	$0.10\times0.05\times0.04$ mm^3
Formula weight	252.69 g/mol
Temperature	294(1) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a=5.4724(3)$ Å $b=5.6742(3)$ Å $c=7.8866(4)$ Å γ=90.361(1)
Volume	244.89(2) Å3
Z	2
Density (calculated)	4.695 mg/m3
Absorption coefficient	5.927 mm^{-1}
Reflections collected	3208
Independent reflections	613 [R(int) = 0.0255]
Absorption correction	Semi-empirical from equivalents
Data/restraints/parameters	613/0/49
Goodness-of-fit on F^2	1.074
Final R indices	$R_1=0.0236$, $wR_2=0.0605$
Largest diff. peak and hole	0.487 and −0.917 e. Å-3

$R(F)^a=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_w(F_o^2)^b=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table 2 Selected interatomic distances for Na_3GaF_6

Ga(1)–F(2)	1.879(2)
Ga(1)–F(2)	1.879(2)
Ga(1)–F(1)	1.887(2)
Ga(1)–F(1)	1.887(2)
Ga(1)–F(3)	1.889(2)
Ga(1)–F(3)	1.889(2)
Na(1)–F(2)	2.235(2)
Na(1)–F(2)	2.235(2)
Na(1)–F(1)	2.285(2)
Na(1)–F(1)	2.285(2)
Na(1)–F(3)	2.293(2)
Na(1)–F(3)	2.293(2)
Na(2)–F(1)	2.281(2)
Na(2)–F(3)	2.290(2)
Na(2)–F(2)	2.304(2)
Na(2)–F(1)	2.363(2)
Na(2)–F(3)	2.609(2)
Na(2)–F(2)	2.667(2)
Na(2)–F(2)	2.741(2)
Na(2)–F(3)	2.876(2)

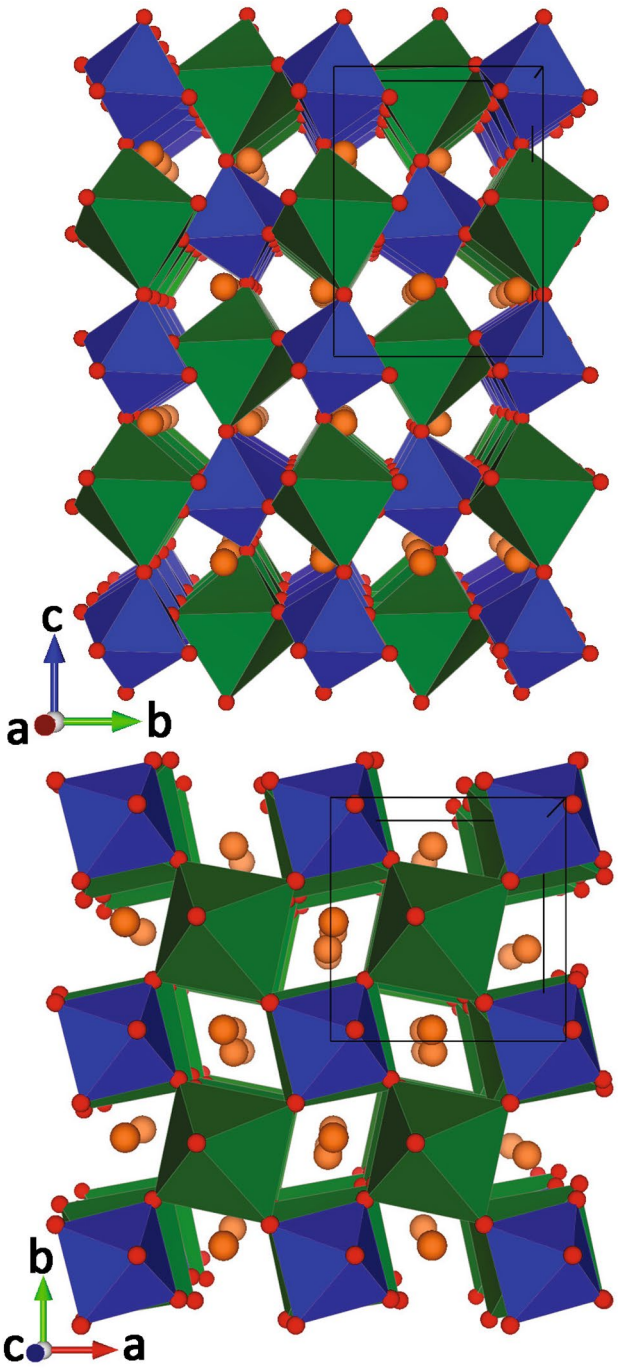

Fig. 1 Polyhedral representation of Na_3GaF_6 along the (*top*) *a*- and (*bottom*) *c*-axis. The corner-shared GaF_6 and $Na(1)F_6$ polyhedra build up a three-dimensional framework, wherein the Na(2) cations reside. The *blue, green, orange*, and *red* polyhedra/spheres represent the Ga, Na(1), Na(2) and F atoms, respectively. (Color figure online)

fluoride compounds have been traditionally prepared by high temperature reactions including solid-state method or flux growth [4–8], hydrothermal process can also provide an effective synthetic route for the synthesis of the fluoride materials at a relatively mild reaction condition [9–11]. In the course of our research for uranium fluorides, Na_3GaF_6 was crystallized through hydrothermal reactions. Although there is a report on the preparation of Na_3GaF_6 powder by

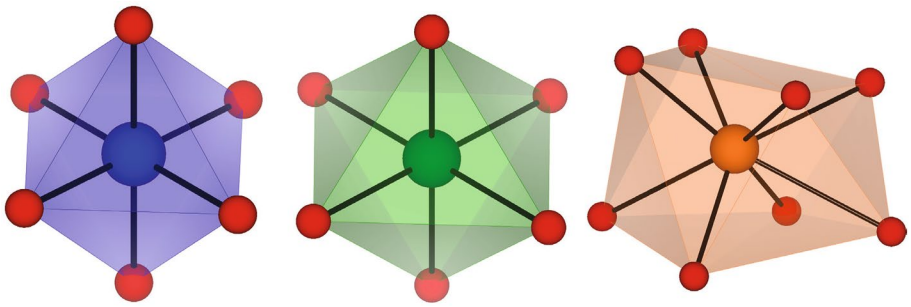

Fig. 2 Illustration of the local coordination environments of the metal atoms. The Ga and Na(1) atoms are located at nearly regular octahedra, whereas the Na(2) is found in a highly distorted antisquare prism. The *blue, green, orange*, and *red* polyhedra/spheres represent the Ga, Na(1), Na(2) and F atoms, respectively. (Color figure online)

mechanochemical method that utilize a ball milling process [12], the crystal structure has not been analyzed yet. In this paper, we report on the hydrothermal synthesis and crystal structure of Na_3GaF_6.

Experimental

Materials and Method

Single crystals of Na_3GaF_6 were grown by a mild hydrothermal route during reactions to prepare $Na_3GaU_6F_{30}$ which is published elsewhere [13]. For the synthesis, 1 mmol of $UO_2(CH_3CO_2)_2{\cdot}2H_2O$, 2 mmol of Ga_2O_3, and 1 mmol of NaF were combined with 1 mL of H_2O and 1 mL of HF. The reaction mixture was placed into 23 mL Teflon–lined autoclaves. The autoclaves were closed, heated to 200 °C at a rate of 5 °C m^{-1}, held for 1 day, and cooled to room temperature at a rate of 6 °C h^{-1}. The mother liquor was decanted from the single crystal products, which were isolated by filtration and washed with distilled water and acetone. Colorless crystals of Na_3GaF_6 were found from the reaction as a minor phase.

Crystallographic Study

X-ray intensity data from a colorless polyhedral crystal (approximate dimensions $0.10\times0.05\times0.04$ mm^3) were measured at 294(1) K on a Bruker SMART APEX CCD diffractometer (Mo Kα radiation, $\lambda=0.71073$ Å) [14]. The raw area detector data frames were reduced with SAINT+ [14]. Data were corrected for absorption effects using the multi-scan technique implemented in SADABS [14]. The reported unit cell parameters were determined by least-squares refinement of large sets of strong reflections taken from each data set. Full-matrix least-squares refinement against F^2 of the structural models and difference Fourier calculations were performed with SHELXTL [15].

The most important crystallographic data and selected interatomic distances from the single crystal structure refinements for Na_3GaF_6 are found in Tables 1 and 2, respectively.

Results and Discussion

Na_3GaF_6 crystallizes in the monoclinic space group $P2_1/n$, and is isostructural with Na_3AlF_6 [16] that belongs to the cryolite type structure with a general formulae A_3BF_6 (A = Li, Na, K, Rb, Tl, NH_4 and M = Al, Sc, V, Cr, Fe, etc.) (Figs. 1, 2). It is also closely related to a double perovskite structure $A_2BB'O_6$, where the A site includes 8- to 12-coordinated cations and the B and B' sites contain octahedrally coordinated metal cations. In such a way, for the title compound if it is written as Na_2NaGaF_6, the Na(2) atom takes on the A site, and the Na(1) and Ga atoms occupy the B and B' sites. Na_3GaF_6 exhibits a three-dimensional framework consisting of corner-shared alternating $Na(1)F_6$ and GaF_6 polyhedra. The Ga atom is located at a nearly regular octahedron with Ga–F distances of 1.879(2)–1.889(2) Å. The Na(1) atom is also observed in an almost regular octahedron with Na-F distances of between 2.235(2) and 2.293(2) Å, whereas the Na(2) atom is coordinated to nine F atoms creating a highly distorted square antiprism with Na(2)–F lengths ranging from 2.281(2) to 2.876(2) Å. The average angle of Na(1)–Ga–Na(1) and Ga–Na(1)–Ga is approximately 140° that is deviated from 180° for the ideal double perovskite structure, which is likely due to the presence of the small Na(2) cation between the framework, enforcing the GaF_6 and $Na(1)F_6$ polyhedra tilted. Bond valence sum calculation [17, 18] resulted in values of 3.01, 0.97–1.21 for Ga^{3+} and Na^+ ions, respectively, consistent with the expected oxidation states.

Supplementary Material

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany; Fax: +49-7247-808-666; E-mail address: crystdata@fizkarlsruhe.de on quoting the depository number CSD-429,839 for Na_3GaF_6.

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References

1. Ahrens M, Schuschke K, Redmer S, Kemnitz E (2007) Solid State Sci 9:833
2. Zhou Q, Kennedy BJ (2004) J Solid State Chem 177:654
3. Flerov IN, Gorev MV, Grannec J, Tressaud A (2002) J Fluor Chem 116:9
4. Yue Y, Hu Z, Chen C (2008) J Cryst Growth 310:1264
5. Birol Y (2007) J Alloys Compd 443:94
6. Slater PR, Gover RKB (2001) J Mater Chem 11:2035
7. Choy J-H, Kim J-Y, Kim S-J, Sohn J-S, Han OH (2001) Chem Mater 13:906
8. Caramanian A, Souron J-P, Gredin P, de Kozak A (2001) J Solid State Chem 159:234
9. Parhi P, Kramer J, Manivannan V (2008) J Mater Sci 43:5540
10. Wang X, Zhuang J, Peng Q, Li Y (2006) Inorg Chem 45:6661
11. Hua RN, Jia ZH, Xie DM, Shi CS (2002) Chin Chem Lett 13:1021
12. Lu J, Zhang Q, Wang J, Saito F (2004) J Am Ceram Soc 87:1814
13. Yeon J, Smith MD, Morrison G, zur Loye H-C (2015) Inorg Chem 54:2058
14. SMART Version 5.625, SAINT + Version 6.45 and SADABS Version 2.05 (2001) Bruker Analytical X-ray Systems, Inc., Madison
15. SHELXTL Version 6.14 (2000) Bruker analytical X-ray Systems, Inc., Madison
16. Hawthorne FC, Ferguson RB (1975) Can Miner 13:(Pt 4):377
17. Brese NE, O'Keeffe M (1991) Acta Crystallogr B 47:192
18. Brown ID, Altermatt D (1985) Acta Crystallogr B 41:244