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Orientational disorder in sodium cadmium trifluoride trihydrate, $NaCdF_3 \cdot 3H_2O$

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Abstract

Attempts to synthesize the hypothetical anhydrous fluoroperovskite $NaCdF_3$, which has been predicted to be stable, resulted instead in a hydrated fluoride of nominal composition $NaCdF_3{\cdot}3H_2O$. It decomposes to sodium fluoride, cadmium fluoride, and water at 60 ºC. Its structure has been determined by single-crystal X-ray diffraction. $Na_{0.92(2)}Cd_{1.08}F_{3.08}{\cdot}2.92H_2O$ crystallizes in the cubic space group $Fm\overline{3}m$ with a = 8.2369(4) Å and Z = 4. The structure is based on the $NaSbF_6$-type (an ordered variant of the ReO_3-type) and features tilted sodium- and cadmium-centred octahedra that are linked by shared vertices to form a three-dimensional network. Substitutional disorder occurs on the nonmetal site, which is occupied by both F and O atoms, and on one of the metal sites, which is occupied by 92% Na and 8% Cd. A four-fold orientational disorder of the tilted octahedra is manifested as partial occupancy (25%) of the nonmetal site. A scheme to synthesize the anhydrous fluoride is presented.

Keywords: A. Fluorides; B. Crystal Growth; C. X-ray Diffraction; D. Crystal Structure

1. Introduction

Perovskites constitute a very important niche within materials science, being used in such applications as ferroelectrics, piezoelectrics, and frequency converters. Each of these applications requires the material to be acentric, i.e., to have no center of symmetry. Fluoroperovskites, with the general formula ABF_3, constitute a subcategory distinguished by being more ionic than the oxide perovskites, which are the most common type of perovskite materials used in technological applications. The greater electronegativity of fluorine compared to oxygen results in a larger band gap for fluoroperovskites than for oxide perovskites and a corresponding absorption edge further into the ultraviolet region [1]. Acentric fluoroperovskites should thus be useful for frequency conversion by second harmonic generation in the ultraviolet region.

The stability of fluoroperovskites (as with any perovskite) is roughly judged by the Goldschmidt tolerance factor, $\tau = (r_A + r_X) / \sqrt{2} (r_B + r_X)$, where r_A, r_B, and r_X are the ionic radii of the large cation, small cation, and anion, respectively [2]. Perovskites with a tolerance factor equal to one will have the ideal cubic perovskite structure. Perovskite materials with tolerance factors less than one become increasingly unstable in the cubic symmetry and distort by various modalities to tetragonal, orthorhombic, or rhombohedral structures, though with the same vertex-sharing arrangement of B-centered octahedra as in the cubic structure [3]. Below a particular tolerance factor, a material will no longer crystallize in any perovskite-related structure. For example, $RbCaF_3$ has a cubic perovskite structure at room temperature [4] whereas $RbSrF_3$ does not form at all, and in the homologous series ACdF$_3$ (A = K, Tl, Rb, Cs), the room-temperature structure is orthorhombic for $KCdF_3$ [5] but cubic for the others [6]. Table

1 shows the tolerance factors, calculated using the effective ionic radii reported by Shannon [7], for some ABF_3 compounds.

Sodium cadmium trifluoride, $NaCdF_3$, has a tolerance factor slightly higher than that of $NaCaF_3$, a material not yet prepared but predicted by computer simulations to be a ferroelectric material and to be isostructural with $LiNbO_3$ [8]. A recent report predicts that $NaCdF_3$, if made, would have a distorted perovskite structure at room temperature, either orthorhombic or rhombohedral, the structures being degenerate and about 60 meV below the energy of the separate binary fluorides, implying chemical stability [9]. Furthermore, either structure would be ferroelectric, with a room-temperature polarization of 0.23 C/m^2 in the rhombohedral and 0.11 C/m^2 in the orthorhombic form, and would have a band gap of 8.5 eV, corresponding to an absorption edge of about 150 nm. In contrast, no fluoroperovskite listed in Table 1 is ferroelectric.

To date, we have been unable to prepare anhydrous $NaCdF_3$ by standard solid-state techniques. Direct combination at high temperatures yields NaF and CdF_2 as determined by X-ray diffraction. A solution route, however, affords the hydrated fluoride of nominal composition $NaCdF_3{\cdot}3H_2O$. Herein we report its structure and thermal properties, and discuss their implications on how the anhydrous fluoroperovskite could be prepared.

2. Experimental

2.1 Synthesis

$NaCdF_3{\cdot}3H_2O$ was prepared by evaporating the solvent from either methanol or aqueous solutions containing equal molar concentrations of NaF and CdF_2; the methanol solutions presumably afforded waters of hydration from atmospheric water vapor. The resulting crystalline solid was examined by powder X-ray diffraction on a Scintag Model PAD V powder diffractometer equipped with Cu Kα radiation and a graphite monochromator. The product was single phase, contained neither NaF nor CdF_2, and was identical in all respects whether made from methanol or aqueous solutions.

2.2 Thermal Analysis

Thermal properties were determined by differential scanning calorimetry conducted on a DuPont Thermal Analyzer 2000. A 25-mg sample was placed in an aluminum pan and heated from room temperature to 200 ºC at 10 ºC/minute. A large endothermic peak occurred at 60 ºC. Mass change upon heating a 30-g sample to 200 ºC indicated 2.8 waters of hydration per formula unit if the anhydrous chemical formula is assumed to be $NaCdF_3$. Powder X-ray diffraction analysis of the sample after heating revealed it to be a mixture of NaF and CdF_2.

2.3 X-ray Diffraction

After several regularly shaped crystals mounted on fibers were screened for integrity, a specimen was chosen on which intensity data were collected by single-crystal X-ray diffraction on a Bruker Platform / SMART 1000 CCD diffractometer equipped with Mo Kα radiation. Crystal data are shown in Table 2. Calculations were carried out with the SHELXTL (version 5.10) package [10]. Face-indexed numerical absorption corrections were applied. The centrosymmetric space group $Fm\bar{3}m$ was chosen and initial atomic positions for Na, Cd, and F/O were easily located by direct methods at Wyckoff sites 4*b*, 4*a*, and 96*k*, respectively. The atomic positions were standardized with the program STRUCTURE TIDY [11]. On the basis of the nominal formula $NaCdF_3 \cdot 3H_2O$ and the similarity of the scattering factors for F and O, the

96*k* site was initially fixed to have a partial occupancy of 0.25 with equal numbers of F and O atoms (i.e., occupancies of 0.125 F and 0.125 O). In the course of the structure refinement, a low displacement parameter at the Na site was found, implying that there was greater electron density there than presumed. Contamination by potassium was ruled out because an EDX (energy-dispersive X-ray) analysis revealed only the presence of Na, Cd, F, and O. Given that Na–F and Cd–O distances are similar (2.35 Å from Shannon ionic radii for CN6), a refinement was performed in which the 96*k* site was allowed to be occupied by a mixture of Na and Cd atoms. The occupancies converged to 0.92(2) Na and 0.08(1) Cd, the displacement parameter became more reasonable, and $R(F)$ (for $F_o^2 > 2\sigma(F_o^2)$) improved from 0.031 to 0.016. To maintain charge neutrality, the formula was revised to $Na_{0.92}Cd_{1.08}F_{3.08}\cdot 2.92H_2O$ and the occupancies of the 96*k* site with F and O atoms were fixed accordingly. Hydrogen atoms were not refined. In the final refinement, the difference electron density map was featureless. Final values of the positional and displacement parameters are given in Table 3. A calculated powder diffraction pattern precisely matched the experimental diffraction pattern.

3. Results and discussion

The hydrated fluoride of nominal composition $NaCdF_3\cdot 3H_2O$ decomposes to NaF, CdF_2, and H_2O at 60 ºC. As determined by the X-ray diffraction study, the solid-solution formula $Na_{0.92}Cd_{1.08}F_{3.08}\cdot 2.92H_2O$ results from the occurrence of two types of disorder in the crystal structure. Substitutional disorder is manifested by 8% Cd substitution on the Na sites and by the mixing of F and O atoms on the nonmetal sites. Fluorine is present as F^- anions and oxygen as belonging to H_2O molecules. Slightly more F than O atoms are present to give the additional negative charge required to balance the excess Cd cations substituted on the Na site.

Orientational disorder of the metal-centred polyhedra in the structure is related to the partial occupancy (25%) of the nonmetal sites. For simplicity, we refer to the compound by its ideal formula $NaCdF_3{\cdot}3H_2O$ in the subsequent discussion.

As shown in Fig. 1(a), the structure consists of a rocksalt arrangement of the Na and Cd atoms with nonmetal sites (*X*) in the intervening space. Each Na and Cd site has 24 equivalent nonmetal sites within the coordination sphere, of which only 1/4 are occupied, resulting in sixfold coordination on a local level. Fig. 1(b) shows one possible local site occupation of nonmetal atoms around a Cd atom to give octahedral coordination geometry (with bond angles of 83.9(2)º and 96.1(2)º). A similar picture applies to the Na atom, which is also octahedrally coordinated (with bond angles of 84.3(2)º and 95.7(2)º). The interpretation is that these Na- and Cd-centred octahedra are tilted so that the metal–*X* bonds are aligned 26.4(2)º and 27.4(2)º away, respectively, from the <100> directions in a random fashion among four possible orientations. No supercell structure was detected, at least for temperatures at or above 193 K, the temperature at which diffraction data were collected.

The metal-centred octahedra are connected through shared vertices to give a three-dimensional framework. The structure can be regarded as a distortion of the $NaSbF_6$-type (an ordered variant of the ReO_3-type), in which the metal-centred octahedra are arranged linearly in all three dimensions, with ideal Na–F–Sb bond angles of 180º [12,13]. In contrast, the Na–*X*–Cd bond angle is significantly smaller at 126.2(2)º in $NaCdF_3{\cdot}3H_2O$. This distortion is similar to that seen in the hexafluorophosphate salts KPF_6 and $CsPF_6$, where a four-fold orientational disorder of octahedra must also be invoked [14]. A related case where substitutional and orientational disorder occur has been recently reported for ammonium elpasolites such as $(NH_4)_2TiOF_5$ [15]. The Na–*X* distances (2.351(3) Å) are shorter than the Cd–*X* distances

(2.268(3) Å), consistent with the larger radius of Na^+ compared to Cd^{2+}. Calculation of bond valence sums [16] nicely corroborates the assignment of the metal and nonmetal atoms. With each metal centre bonded to three F and three O atoms, the bond valence sums are 1.1 for the Na site and 2.0 for the Cd site. Each O atom is bonded to one Na, one Cd, and two H atoms (at ~1.0 Å), yielding a bond valence sum of 2.0. It can also be concluded that each F atom must be bonded to at least one H atom (at ~1.1 Å), in addition to one Na and one Cd atom, in order to attain a reasonable bond valence sum of 1.0. Hydrogen bonding interactions (O–H···O and O–H···F) are thus quite extensive in this structure.

4. Concluding Remarks

Although the preparation of the hydrated fluoride $NaCdF_3 \cdot 3H_2O$ was unintended, it helps provide insight into possible means to produce the anhydrous fluoroperovksite $NaCdF_3$, which was the originally targeted compound. That the trihydrate, when it is dehydrated, collapses into the binary fluorides rather than into the fluoroperovskite implies that no stable atomic-rearrangement pathway exists to go from the hydrate to the anhydrous fluoroperovskite. It is therefore unlikely that the anhydrous material can be prepared under equilibrium conditions; rather, some sort of kinetically favorable synthetic route will be required. One possibility is to use thin-film deposition on a substrate with a lattice and orientation appropriate to the structure of the desired material. A suitably well-matched substrate provides a template upon which even a thermodynamically unstable material can grow. For example, $YMnO_3$ with a distorted perovskite structure has been grown as a thin film even though its thermodynamically stable structure is a non-perovskite type [17]. A thin-film technique such as pulsed laser deposition, which provides a stoichiometric transfer of elements from target to substrate, may prove suitable for synthesis of the anhydrous fluoroperovskite.

Acknowledgments

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References

[1] C. Fouassier, Optical properties of fluorides, in: P. Hagenmuller (Ed.), Inorganic Solid Fluorides, Academic Press, Orlando, Florida, 1985, pp. 477–487.

[2] V.M. Goldschmidt, Naturwissenschaften 14 (1926) 477.

[3] A.M. Glazer, Acta Crystallogr., Sect. A 31 (1975) 756.

[4] A. Ratuszna, P. Daniel, M. Rousseau, Phase Transitions 54 (1995) 43.

[5] M. Hidaka, S. Hosogi, J. Phys. (Paris) 43 (1982) 1227.

[6] M. Rousseau, J.Y. Gesland, J. Julliard, J. Nouet, J. Zarembowitch, A. Zarembowitch, Phys. Rev. B 12 (1975) 1579.

[7] R.D. Shannon, Acta Crystallogr., Sect. A 32 (1976) 751.

[8] P.J. Edwardson, L.L. Boyer, R.L. Newman, D.H. Fox, J.R. Hardy, J.W. Flocken, R.A. Guenther, W.N. Mei, Phys. Rev. B 39 (1989) 9738.

[9] C. Duan, W.N. Mei, J. Liu, W.-G. Yin, J.R. Hardy, R.W. Smith, M.J. Mehl, L.L. Boyer, Phys. Rev. B 69 (2004) 033102/1.

[10] G.M. Sheldrick, SHELXTL, Version 5.10, Bruker AXS Inc., Madison, WI, 1998.

[11] L.M. Gelato, E. Parthé, J. Appl. Crystallogr. 20 (1987) 139.

[12] G. Teufer, Acta Crystallogr. 9 (1956) 539.

[13] H. Sowa, Acta Crystallogr., Sect. B 53 (1997) 25.

[14] K. Kitashita, R. Hagiwara, Y. Ito, O. Tamada, J. Fluorine Chem. 101 (2000) 173.

[15] A.A. Udovenko, N.M. Laptash, I.G. Maslennikova, J. Fluorine Chem. 124 (2003) 5.

[16] N.E. Brese, M. O'Keeffe, Acta Crystallogr., Sect. B 47 (1991) 192.

[17] P.A. Salvador, T.-D. Doan, B. Mercey, B. Raveau, Chem. Mater. 10 (1998) 2592.

Table 1

Tolerance factors for fluoroperovskites (*AB*F_3) [a]

	Mg^{2+}	Zn^{2+}	Cd^{2+}	Ca^{2+}	Sr^{2+}	Pb^{2+}	Ba^{2+}
Na^{+}	0.938	0.929	<u>0.844</u>	<u>0.825</u>	<u>0.766</u>	<u>0.763</u>	<u>0.718</u>
K^{+}	1.024	1.015	0.921	0.901	<u>0.837</u>	<u>0.833</u>	<u>0.784</u>
Tl^{+}	1.045	1.035	0.940	0.920	<u>0.854</u>	<u>0.850</u>	<u>0.799</u>
Rb^{+}	1.052	1.042	0.946	0.926	<u>0.859</u>	<u>0.856</u>	<u>0.805</u>
Cs^{+}	1.107	1.097	0.996	0.974	0.904	0.901	<u>0.847</u>

[a] Calculated from Shannon effective ionic radii for A^{+} (CN12), B^{2+} (CN6), and F^{-} (CN6) ions. Tolerance factors are underlined for compounds not known to exist.

Table 2

Crystallographic data for $Na_{0.92}Cd_{1.08}F_{3.08}\cdot 2.92H_2O$

Formula mass (amu)	253.67
Space group	O_h^5–$Fm\overline{3}m$ (No. 225)
a (Å) [a]	8.2369(4)
V (Å^3)	558.85(5)
Z	4
ρ_{calcd} (g cm^{-3})	3.015
Crystal dimensions (mm)	0.31 × 0.15 × 0.09
Radiation	Graphite monochromated Mo $K\alpha$, λ = 0.71073 Å
μ(Mo $K\alpha$) (cm^{-1})	42.65
Transmission factors	0.435–0.687
2θ limits	8.58° ≤ 2θ(Mo $K\alpha$) ≤ 66.14°
Data collected	$-12 \le h \le 12$, $-12 \le k \le 12$, $-12 \le l \le 12$
No. of data collected	1834
No. of unique data, including $F_o^2 < 0$	79
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	79
No. of variables	10
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [b]	0.012
$R_w(F_o^2)$ [c]	0.028
Goodness of fit	1.28
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	0.48, –0.44

[a] Obtained from a refinement constrained so that $a = b = c$ and $\alpha = \beta = \gamma = 90°$.

[b] $R(F) = \sum \left\| F_o \right| - \left| F_c \right\| / \sum \left| F_o \right|$.

[c] $R_w(F_o^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.02p)^2]$ where

$p = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table 3

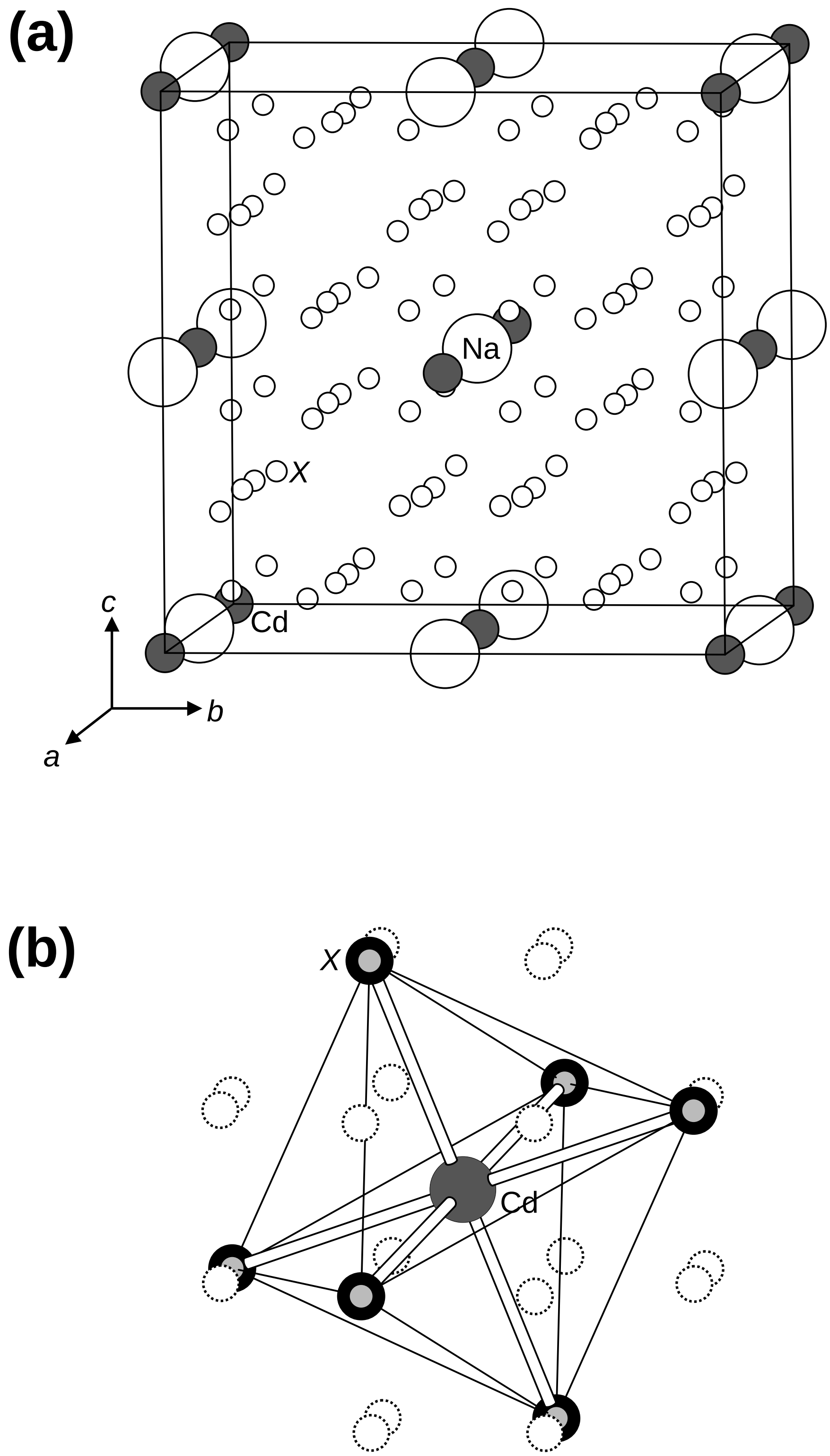
Atomic coordinates and equivalent isotropic displacement parameters for $Na_{0.92}Cd_{1.08}F_{3.08}\cdot 2.92H_2O$

Site	Wyckoff position	Occupancy	*x*	*y*	*z*	U_{eq} (Å^2) [a]
A	4*b*	0.92 Na, 0.08 Cd	1/2	1/2	1/2	0.0134(3)
B	4*a*	1.00 Cd	0	0	0	0.0101(2)
X	96*k*	0.13 F, 0.12 O	0.0897(3)	*x*	0.2444(3)	0.0155(5)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Figure captions

Fig. 1. (a) Unit cell of $NaCdF_3{\cdot}3H_2O$. The large open circles are Na atoms, the medium solid circles are Cd atoms, and the small open circles are nonmetal sites *X*, partially occupied (25%) by a mixture of F and O atoms. (b) One of four possible orientations of the Cd-centred octahedron, generated by local occupation of 1/4 of the nonmetal sites in sixfold coordination.


(a)
Na
X
Cd
c
b
a
(b)
X
Cd